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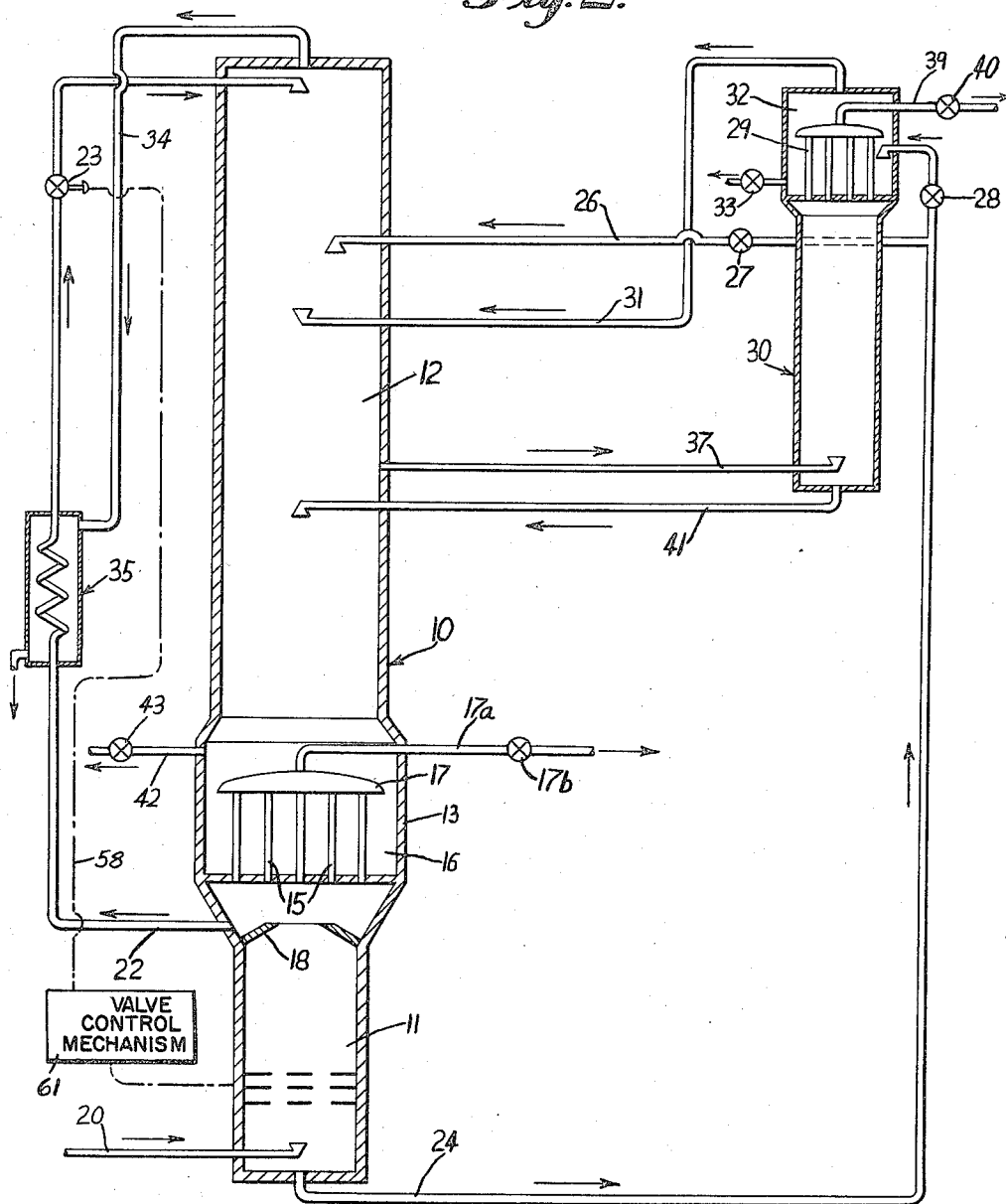
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HIGH ARGON RECOVERY USING PROPER SHELF-TOP PINCH PRINCIPLE

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2 Sheets-Sheet 2

Fig. 2.



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HIGH ARGON RECOVERY USING PROPER SHELF-TOP PINCH PRINCIPLE**Robert E. Latimer, Kenmore, N.Y., assignor to Union Carbide Corporation, a corporation of New York****Application August 16, 1954, Serial No. 449,938****15 Claims. (Cl. 62--22)**

This invention relates to a process of separating low boiling ternary gas mixtures and more particularly to the recovery of argon by low temperature separation of air.

Most of the argon used in the world is produced as a by-product in the production of oxygen by low temperature separation of atmospheric air into its major constituents. It has not been found practical or economical to produce it otherwise. But known oxygen plants have a relatively low argon producing capacity because a sizable fraction of the argon in the air treated is lost in the effluent nitrogen. With the greatly increased consumption of argon in recent years, presently employed processes and plants have not been able to meet the increased demands without incurring an overproduction of oxygen.

The recovery of an argon product when separating air by low temperature rectification has been accomplished by withdrawing fluid from an intermediate zone of a final rectification, where the argon concentration is high and nitrogen concentration is low, and then subjecting the withdrawn fluid to auxiliary rectification. Although argon in a state of high purity has been obtained in this manner, known processes of this type have not functioned efficiently with respect to the production of argon and only a relatively low percentage of the argon present in each unit volume treated has been recovered, the unrecovered argon being lost with the oxygen and nitrogen products.

The primary object of this invention, therefore, is to provide an improved process for obtaining increased producing capacity in existing and new equipment in the production of an intermediate boiling point component in the separation of a ternary gas mixture. More particularly, the present invention has for its object to obtain increased recovery efficiency in the production of argon in air separating processes recovering both oxygen and argon. Another object of the present invention is to reduce the unit cost of argon production.

Still another object of the invention is to provide new features of control to maintain stabilized operation of the process mentioned hereinabove.

The foregoing and other objects of this invention are brought about according to the invention by making use of several correlatable principles which include:

First, that the upper part of the low pressure stage of a well known double rectification column can be made to trap argon, which has heretofore left the column with the effluent waste nitrogen top product and has been lost, and to wash such argon down the column to a zone where the fluid has relatively high argon content and very low nitrogen content. The argon trap is produced by applying an "oxygen-pinch" to the top of the low pressure rectification stage where nitrogen-rich reflux liquid is introduced, as well as to other feed points in the upper column above the argon take-off. At these zones, particularly the top zone where the oxygen-nitrogen pinch is coldest because of the cold nitrogen liquid being introduced thereinto, the oxygen-nitrogen ratio driving force is very small and the argon-nitrogen ratio driving force can be utilized to effect

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a washing down of the argon out of the waste nitrogen top product.

In the rectification art, a "pinch" refers to a reflux condition where the contacting liquid and vapor are in substantial equilibrium, there being little driving force for rectification and there being required several trays to effect a small composition change. As herein employed, an "oxygen-pinch" may be defined as a reflux condition where there is a zone including several trays over which practically no change in the oxygen content of the descending liquid occurs but an effective change in the argon content is maintained. Accordingly, the application of an "oxygen-pinch" at the top of the low pressure rectification stage just below the top feed point, and just below the other feed points thereof, to produce an argon trap where argon is washed out of the rising vapor is hereinafter referred to as the "top oxygen-pinch" principle.

Second, that in the separation of air by a two stage rectification wherein nitrogen-rich reflux liquid and oxygen-enriched reflux liquid are introduced into the second rectification stage, the proper "top oxygen-pinch" can be applied by regulation of the argon content and oxygen content in the refluxing nitrogen-rich liquid introduced in the low pressure stage of the rectifying column. In other words, most favorable argon recoveries have been obtained by using a nitrogen-rich washing liquid at the top of the low pressure rectification stage that is relatively free of argon, but has proper oxygen content to effect equilibrium conditions favorable to argon enrichment and unfavorable to oxygen enrichment.

Third, that, in liquid oxygen plants, limiting and adjusting the purity of the effluent nitrogen and of the nitrogen-rich reflux liquid minimizes reduction in argon content of the descending liquid at the bottom of the top part of the upper column in the region of oxygen enrichment just above the oxygen liquid feed, where equilibrium conditions are unfavorable to argon enrichment, and accordingly increases the total amount of argon passing to the lower part of the upper column where argon is removed.

According to a preferred embodiment of this invention, the "top oxygen-pinch" principle is applied to liquid oxygen producing double column rectification units of known type by regulating the transfer throttling valve through which the refluxing nitrogen-rich transfer liquid is passed so that such liquid, when introduced into the top of the upper, low pressure column, has a minimum content of argon and sufficient oxygen content to achieve equilibrium with the effluent nitrogen, and by employing a sufficient quantity of such transfer liquid so that in a region including several trays at the top of the column a pinch is produced where there is practically no change in the low oxygen content of the descending liquid. In general, setting aside some trays for this region increases the total number required in this unit. It is also desirable to establish other oxygen pinches at the upper part of the column just below the upper feed points by introducing oxygen enriched reflux liquid and oxygen enriched vapor at appropriate, determinable points in the upper part of such column.

In practice the effectiveness of such oxygen pinches is indicated by the composition difference between trays just below the various feed points. Accordingly, purity measurement, either directly or indirectly as by temperature measurement, provides a gauge for exercising suitable control of the oxygen pinches. It will be observed that as the purity of the effluent nitrogen varies, i.e. more or less oxygen escapes with the waste nitrogen and less or more is taken out of the system as liquid oxygen, the refrigeration required to generate vapor having a desired argon content varies. Therefore, control

of the reflux ratio in the upper low pressure column to maintain a substantially constant argon content at the argon take off provides a stable operation of the system.

In another embodiment of the invention, the "top oxygen-pinch" is applied to an oxygen gas producing plant. Here, substantially the entire air supply is passed to the lower, high pressure chamber of the double rectification column as vapor thus eliminating the necessity of limiting the purity of the effluent nitrogen to avoid an undesirable equilibrium pinch at the bottom of the top part of the upper column, and thus enabling a much higher reflux or liquid-vapor ratio to be used in the lower column that results in a wash-out of nearly all the oxygen and argon from the nitrogen rich transfer liquid. Accordingly, the upper column is provided with a sufficient number of trays to raise the purity of the effluent nitrogen to approach a condition of equilibrium with the refluxing nitrogen transfer liquid so as to generate an oxygen pinch at the top of the upper column.

These and other objects, features and advantages of the present invention will become apparent from the following detailed description of the accompanying drawings in which:

Fig. 1 shows in conventional diagrammatic form air separation apparatus illustrating the principles of the improved process as applied to a plant wherein an argon fraction, a nitrogen fraction, and a substantially pure liquid oxygen fraction are produced; and

Fig. 2 shows in conventional diagrammatic form air separation apparatus illustrating another embodiment of the improved process as applied to a plant producing an argon fraction, a nitrogen fraction and a gaseous oxygen product of high purity.

The present invention will be described in connection with the apparatus of Fig. 1 which is particularly suitable for the separation of air to obtain a liquid oxygen product substantially free of higher boiling point impurities and a product having a high content of argon. However, modifications within the scope of the invention may be made as exemplified in Fig. 2, if it is desired, to recover the oxygen product in gaseous rather than in liquid form.

Referring now to Fig. 1 of the drawing, the air rectifying apparatus, except as explained hereinafter, is generally of conventional construction and includes a double column, indicated at 10, having the usual high pressure stage chamber or lower column 11, a low pressure stage chamber or upper column 12 extending above the lower column, and main condenser 13 disposed between the two columns and sealing the high pressure chamber 11 from the low pressure chamber 12. The high and low pressure chambers may contain customary column trays, such as perforated plates 14, which effect intimate contact with vapors rising in the column and reflux liquid flowing down the column. The main condenser 13 is provided with vertical tubes 15, disposed in a liquid oxygen collecting chamber 16 at the bottom part of the upper column, the lower ends of these tubes opening into the upper end of the high pressure rectification chamber 11 to receive the vapor used in the rectifying action of the lower column and effect a condensing of such vapor by the action of relatively cold oxygen liquid in chamber 16 of the upper column. The upper ends of the tubes open into a sealing dome 17, from which nitrogen rich gas may be taken off, as desired, through a conduit 17a by operation of a control valve 17b. An annular shelf 18 is disposed in high pressure chamber 11 in a position underlying the radially outer tubes of the main condenser 13 for catching and collecting high purity condensed nitrogen falling from such tubes.

The bottom of the upper column or low pressure rectifying chamber 12 opens into the liquid oxygen collecting chamber of the main condenser 13 for effecting the boil-

ing of part of liquid oxygen collected therein to produce vapor for the rectifying action in the upper column. The oxygen boils at the low pressure of the upper column at a temperature which is lower than the condensing temperature of the nitrogen in the condenser which is under the pressure of the lower column.

Cooled and cleaned air under a compression of about 80 p.s.i. is fed into the bottom part of the lower column 11 through a conduit 20. This air is subjected to an initial rectification whereby an oxygen rich liquid fraction is produced that accumulates at the base of the lower column and a nitrogen rich gaseous fraction is produced at the top of the lower column. The nitrogen rich gas enters the tubes 15 of the main condenser 13 and is partially condensed, the condensed fraction falling back into lower column where part is received on annular shelf 18 and part is received on the top trays to serve as reflux liquid for the lower column. The vapor fraction of the nitrogen rich gas passing out of the condenser enters and accumulates in the sealing dome 17 where it can be drawn off as desired through conduit 17a as mentioned above.

The nitrogen rich liquid collected on shelf 18 is withdrawn from the lower column through a conduit 22 and passed through a heat exchanger 35 in heat exchange relationship with effluent nitrogen gas leaving the upper column 12 through a conduit 34. After it has been cooled by the effluent nitrogen it traverses a throttling valve 23 where reduction in pressure results in a further drop in temperature. It is then passed into the top of the upper column at rates controlled by the expansion valve 23 to provide cold nitrogen rich reflux liquid of a desired purity.

The oxygen enriched liquid that accumulates at the base of the lower column is withdrawn through a conduit 24 and is passed through filters 25. The clean liquid is then split, a portion being introduced directly into the upper column by a conduit 26 controlled by throttling valve 27 and the remainder being passed through a throttling valve 28 to a chamber 32 surrounding a condenser 29 in the top part of an auxiliary rectifying column 30. The oxygen rich liquid entering such column is vaporized and passed through a conduit 31 into the upper column for further rectification.

A liquid oxygen product may be withdrawn at a valved outlet 36.

At this point it may be explained that in order to apply the "top oxygen-pinch" according to the principles of this invention, it is necessary to provide a section at the top of the upper column where the reflux liquid is used principally to wash argon from the rising vapor.

Referring now in particular to the operation of the upper or main rectification column, an oxygen pinch region in the upper part of the column that is favorable to argon enrichment in such upper part, without producing objectionable blocks to the washing down of argon at lower areas of the column, is obtained by maintaining a relatively low nitrogen purity of about 98.5% in the effluent nitrogen product and using a relatively low nitrogen purity of about 96% in the reflux liquid introduced at the top of the column. Of the pinches produced at the various feed points, the uppermost one is the most important with respect to high argon recovery, for it is in this top part of the column that the nitrogen rich liquid is coldest and the equilibrium conditions produced by the refluxing nitrogen rich liquid are most favorable to argon enrichment. The refluxing liquid required to produce this top pinch is obtained by regulation of valve 23, which controls the rate of transfer of nitrogen rich liquid collected on shelf 18 to the upper column, so as to introduce into the top of the upper column through conduit 22 nitrogen rich liquid having sufficient oxygen content to effect an oxygen-nitrogen equilibrium condition at the top region of the

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column while maintaining a favorable argon enrichment condition.

Other oxygen pinches in the upper part of the upper column, which enhance the wash-out of argon from the rising vapor are provided by proper location of the feed conduits 26 and 31, respectively, to introduce oxygen enriched liquid and oxygen enriched vapor at points producing substantial oxygen-nitrogen equilibrium conditions in the column at these points.

An indication of the effectiveness of the pinches is obtained by a purity measurement, taken directly or indirectly as by temperature measurement, below any of the various feed points. In practice one suitable way of holding desired pinches is to maintain a predetermined difference in the oxygen content of the vapor on the second and third trays below the oxygen enriched vapor feed point by controlling the argon production rate. For example, in a liquid oxygen plant to which the principles of the invention have been applied, it has been found that by holding about a 1.4% difference in the oxygen content on these trays, a sufficient pinch was produced to wash down a high percentage of the argon in the rising vapor and to pass such argon down the column to a point where it can be recovered. In this way a high recovery of argon can be achieved while still producing a substantial yield of high purity oxygen. The measurement of the difference in the oxygen content of the vapor on the second and third trays below the oxygen-enriched vapor feed point may be accomplished by temperature changes sensed by thermometers 50. The temperature changes registered thereby activate valve control mechanism in the pinch controller 51 which is connected by line 52 to valve 40 in conduit 39, such valve controlling the argon production rate.

At an intermediate point of the upper column where the vapor has a relatively high content of argon and a relatively low content of nitrogen, a vapor outlet conduit 37 is connected to the column to conduct argon containing vapor into a lower part of auxiliary rectifying column 30. This column has gas and liquid contact means such as trays 38. The argon containing vapor passes upwardly through the column 30 and is washed with a reflux liquid produced by condensation of the rising vapors in condenser 29 at the top of the column. The vapors passing through the tubes of condenser 29 are subjected to partial liquefaction, the liquid produced being rich in argon and forming a suitable reflux liquid for washing down the oxygen out of the rising vapor in the column. The argon-rich vapor that remains uncondensed may be withdrawn through a conduit 39 that is provided with a control valve 40. The liquid which accumulates at the bottom of the auxiliary column is substantially reduced in its argon content and is preferably returned by a conduit 41 to the upper column 12 of the main rectification, being admitted at a point near the argon take off.

Although a large part of the higher boiling point impurities will be removed by filters 25, there is usually a gradual concentration of higher boiling point impurities in the condenser 29 of the auxiliary column, and a drain valve 33 connected to a lower part of the chamber 32 is provided to allow removal of such concentrate at infrequent intervals.

It will be observed that opening valve 23 lowers the purity of the nitrogen rich transfer liquid and consequently lowers the purity of the effluent nitrogen. This increases the oxygen pinch and results in an undesirably large nitrogen content at the argon take off unless the refrigeration supplied to the system is reduced. Accordingly, it is desirable to regulate the refrigeration supplied to the rectification to hold a substantially constant argon content in the vapor at the argon take off. This regulation may be achieved by controlling the reflux ratio in the upper column, as by regulation of oxygen-make withdrawal through conduit 36.

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In the embodiment of Fig. 2, features similar to those already described with reference to Fig. 1 are designated by the same reference numbers. Here the oxygen product is withdrawn from the main condenser 13 through conduit 42 in a gaseous state. The gaseous oxygen withdrawn may be controlled by valve 43.

It will be understood that in an oxygen gas producing plant wherein substantially the entire air supply is passed to the lower column 11 as vapor, a bottom equilibrium pinch known in oxygen liquid producing plants is avoided and there is no problem of avoiding an oxygen pinch at the bottom of the upper section in the upper column which tend to trap descending argon. Thus, in gas plants there is no need to limit the purity of the effluent nitrogen and the upper section can be employed in this type of plant to raise the purity of the waste nitrogen product. In the lower column which receives substantially the entire air supply, a much higher reflux or liquid-vapor ratio can be used to wash nearly all of the oxygen and argon out of the rising vapor so that the nitrogen gas which is condensed in the main condenser 16 and subsequently accumulates on the shelf 18 has a purity approaching that of the effluent nitrogen. For example, in practice a purity of 0.4% oxygen may be attained in the shelf liquid.

In this manner the waste nitrogen gas and the refluxing nitrogen rich liquid entering the top of the column through conduit 22 both contain a very small amount of oxygen and are nearly in equilibrium, thereby producing an oxygen pinch condition over several trays at the top of the column in which there is very little oxygen nitrogen rectification driving force. In this region the argon nitrogen driving force may be employed to effect a wash down of the argon in the rising vapor.

The required top oxygen pinch which results in increased argon recovery may also be sensed by purity conditions, either directly or indirectly as by temperature measurement, below any of the various feed points as in oxygen producing liquid plants. Here also the gauged condition in the column at the observation station is adjusted by controlling the withdrawal of crude argon through line 39. The argon concentration at the take off level may be controlled by the oxygen make withdrawal. A sensing device is placed in the lower column which indicates the proper setting of the transfer valve 23.

It will be understood that changes in carrying out the above described process may be made without departing from the principles of the invention.

What is claimed is:

1. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen which comprises: subjecting air to a two-stage rectification wherein nitrogen-rich reflux liquid and oxygen-enriched flux liquid are introduced into the second rectification stage and wherein an oxygen product and a nitrogen product are formed, washing the rising vapor at the top portion of the second rectification stage with nitrogen-rich reflux liquid having such a composition as to be in oxygen-nitrogen phase equilibrium with the vapor at the reflux liquid feed point to produce an oxygen pinch at the top of this stage where reflux liquid is used principally to wash argon out of the rising vapor, and withdrawing from a zone of the second rectification stage where the argon content is high, a fluid comprising mainly oxygen and argon to be further distilled in an auxiliary rectification.

2. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen which comprises: subjecting air to a two-stage rectification wherein nitrogen-rich reflux liquid and oxygen-enriched reflux liquid are introduced into the second rectification stage and wherein an oxygen make product and a nitrogen product are formed, washing the rising vapor at the top portion of the second rectification stage with nitrogen-rich reflux liquid having such a composition as to be in oxygen-nitrogen phase equilibrium with the vapor at the reflux liquid feed point to produce an oxygen pinch at the top of

this stage where reflux liquid is used principally to wash argon out of the rising vapor, sensing said pinch by taking a purity measurement below one of the points of feed to the upper column, withdrawing from a zone of the second rectification stage where the argon content is high, a fluid comprising mainly oxygen and argon to be further distilled in an auxiliary rectification, to produce an argon product and an oxygen product that is returned to the second rectification stage, and maintaining a predetermined condition of purity at the measuring station by regulating the rate of net argon withdrawal from said zone.

3. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen which comprises: subjecting air to a two-stage rectification wherein nitrogen-rich reflux liquid, oxygen-enriched reflux liquid and oxygen-enriched vapor are introduced into the second rectification stage and wherein an oxygen make product and a nitrogen product are formed, washing the rising vapor at the top portion of the second rectification stage with nitrogen-rich reflux liquid having a composition substantially in oxygen-nitrogen phase equilibrium with the vapor at the reflux liquid feed point so that an oxygen pinch is produced at the top of this stage where reflux liquid is used principally to wash argon out of the rising vapor, sensing said pinch by measuring the difference in the oxygen content of the rising vapor across two rectifying steps just below the oxygen-enriched vapor feed point, withdrawing from a zone of the second rectification stage where the argon content is high, a fluid comprising mainly oxygen and argon to be further distilled in an auxiliary rectification, to produce an argon product and an oxygen product that is returned to said second rectification stage, and regulating the rate of net argon withdrawal from said zone to hold a predetermined difference in the oxygen content across said two rectifying steps so as to maintain said pinch.

4. A process for the separation of air according to claim 1, which includes the step of regulating the rate of oxygen product withdrawal from the bottom of the upper column so as to maintain a substantially constant argon content in the withdrawn fluid.

5. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen, which comprises subjecting air to a two-stage rectification wherein nitrogen-rich reflux liquid and oxygen-enriched reflux liquid are introduced into the second rectification stage and wherein an oxygen product and a nitrogen product are formed, washing the vapor current at the top portion of the second rectification stage with nitrogen-rich reflux liquid having such an oxygen content that the nitrogen and oxygen components of the refluxing liquid and the vapor are substantially in phase equilibrium at the reflux liquid feed point so as to produce an oxygen pinch at the top of this stage, withdrawing from a zone of the second rectification stage where the argon content is high, a vapor comprising mainly oxygen and argon, subjecting such vapor to an auxiliary rectification by washing with a reflux liquid formed by partial liquefaction of vapor of the auxiliary rectification, and producing said reflux by a heat exchange between vapor of the auxiliary rectification and oxygen-enriched liquid withdrawn from the first rectification stage to substantially vaporize such liquid and provide oxygen-enriched vapor.

6. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen which comprises: subjecting air to a two-stage rectification wherein nitrogen-rich reflux liquid and oxygen-enriched reflux liquid are introduced into the second rectification stage and wherein a liquid oxygen product of desired purity and a cold nitrogen product are formed, withdrawing from the first rectification stage and transferring to the top of said second rectification stage nitrogen-rich liquid having a sufficient oxygen content to achieve oxygen-nitrogen phase equilibrium with the rising vapor at

the feed point of such liquid so as to produce an oxygen pinch at the top of said second rectification stage, and withdrawing from a zone of the second rectification stage where the argon content is high, a fluid comprising mainly oxygen and argon to be further distilled in an auxiliary rectification.

7. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen which comprises: subjecting air to a two-stage rectification wherein a liquid oxygen product of desired purity and a cold nitrogen product are formed; washing the top portion of the vapor current of the second rectification stage with a nitrogen-rich reflux liquid transferred from the first rectification stage, introducing oxygen-enriched reflux liquid into the upper portion of the second rectification stage but below said nitrogen rich reflux liquid feed point, transferring from the first rectification stage to the top of said second rectification stage a nitrogen-rich reflux liquid having a sufficient oxygen content to achieve oxygen-nitrogen phase equilibrium with the rising vapor at the feed point of such liquid so as to produce an oxygen pinch at the top of such stage, controlling the oxygen content of said nitrogen-rich reflux liquid by varying the rate at which such liquid is transferred from said first to said second stages, and withdrawing from a zone of the second rectification stage where the argon content is high, a fluid comprising mainly oxygen and argon to be further distilled in an auxiliary rectification.

8. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen which comprises: subjecting air to a two-stage rectification wherein, an oxygen product of desired purity and a cold gaseous nitrogen product are formed, washing the top portion of the vapor current of the second rectification stage with a nitrogen-rich reflux liquid transferred from the first rectification stage having a composition substantially in oxygen-nitrogen phase equilibrium with the rising vapor of said second stage at the feed point of such liquid, introducing oxygen-enriched reflux liquid and oxygen-enriched vapor into the upper part of the second rectification stage at points intermediate an argon-enriched fluid take-off and the nitrogen-rich reflux liquid feed point where substantial oxygen-nitrogen phase equilibrium between liquid and vapor will result so as to produce oxygen pinches in the regions just below each of these feed points and withdrawing from a zone of the second rectification stage where the argon content is high and the nitrogen content is low, a fluid comprising mainly oxygen and argon to be further distilled in an auxiliary rectification.

9. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen which comprises: subjecting air to a two-stage rectification wherein nitrogen reflux liquid and oxygen enriched reflux liquid are introduced into the second rectification stage and wherein a gaseous oxygen product of desired purity and a cold nitrogen product are withdrawn, operating the first, high pressure rectification stage with a high liquid-vapor reflux ratio to produce a nitrogen-rich liquid nearly devoid of oxygen and argon at the top of such first stage, providing sufficient rectification steps in the second low pressure rectification stage to substantially complete oxygen and nitrogen separation and providing excess rectification steps at the top cold end of this second stage, introducing the very high purity nitrogen reflux liquid from said first stage into the top of said second stage to establish an oxygen pinch condition over said excess rectification steps and utilize such reflux liquid principally to wash argon out of the rising vapor passing upwardly through these steps, and withdrawing from a zone of the second rectification stage where the argon content is high, a fluid comprising mainly oxygen and argon to be further distilled in auxiliary rectification to produce an argon product and an oxygen product that is returned to the second rectification stage.

10. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen, which comprises: subjecting air to a two-stage rectification wherein nitrogen-rich reflux liquid and oxygen-enriched reflux liquid are introduced into the second rectification stage and wherein an oxygen product and a nitrogen product are formed, maintaining an oxygen pinch condition at the top zone of the second rectification stage to utilize reflux liquid principally for washing argon out of the rising vapor passing through this top zone, and withdrawing from another zone of the second rectification stage where the argon content is high and the nitrogen content is low, a fluid comprising mainly oxygen and argon to be further distilled in an auxiliary rectification.

11. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen, which comprises: subjecting air to a two-stage rectification wherein nitrogen-rich reflux liquid and oxygen-enriched reflux liquid are introduced into the second rectification stage and wherein an oxygen product and a nitrogen product are formed utilizing an excess of rectifying steps in the second rectification zone over that normally required to separate oxygen and nitrogen, regulating reflux conditions of this second stage so that the excess rectifying steps are at the cold end of said second stage, maintaining an oxygen pinch in the zone of said excess rectifying steps to utilize reflux liquid principally for washing argon out of the rising vapor passing through this zone, and withdrawing from another zone of the second rectification stage where the argon content is high and the nitrogen content is low, a fluid comprising mainly oxygen and argon to be further distilled in an auxiliary rectification.

12. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen, which comprises: subjecting air to a two-stage rectification wherein nitrogen-rich reflux liquid and oxygen-enriched reflux liquid are introduced into the second rectification stage and wherein an oxygen product and a nitrogen product are formed, introducing a reflux fluid into the second stage having such an oxygen content in relation to the oxygen content of the rising vapor at the feed point that an oxygen pinch condition is established in the zone just below the feed point and wherein descending reflux liquid is used principally for washing argon out of the rising vapor passing through this zone, and withdrawing from another zone of the second rectification stage when the argon content is high and the nitrogen content is low, a fluid comprising mainly oxygen and argon to be further distilled in an auxiliary rectification.

13. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen, which comprises: subjecting air to a two-stage rectification wherein nitrogen-rich reflux liquid and oxygen-enriched reflux liquid are introduced into the second rectification stage and wherein an oxygen product and a nitrogen product are formed, introducing a plurality of reflux liquids into the second rectification stage which are in substantial oxygen-nitrogen phase equilibrium with the rising vapor at their respective feed points so as to produce oxygen pinches in the zones just below said feed points and to utilize the reflux liquid passing downwardly through these zones principally for washing argon out of the rising vapor, and withdrawing from another zone

of the second rectification stage where the argon content is high and the nitrogen content is low, a fluid comprising mainly oxygen and argon to be further distilled in an auxiliary rectification.

14. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen, which comprises: subjecting air to a two-stage rectification, under conditions of high liquid-vapor reflux ratios in the first rectification stage, introducing nitrogen-rich reflux liquid substantially devoid of oxygen and argon into the top of the second rectification stage, and utilizing an excess of rectifying steps in the second rectification stage over that normally required to separate oxygen and nitrogen to raise the purity of the effluent to a condition approaching that of the nitrogen-rich reflux, thereby effecting an oxygen pinch condition in the zone of the excess steps of the second rectification stage wherein such reflux is used primarily to wash argon out of the rising vapor, and withdrawing from a zone of the second rectification stage where the argon content is high, a fluid comprising mainly oxygen and argon to be further distilled in an auxiliary rectification.

15. A process for the separation of air by low temperature rectification to obtain oxygen, argon and nitrogen which comprises subjecting air to a two-stage rectification wherein nitrogen reflux liquid and oxygen enriched reflux liquid are introduced into the second rectification stage and wherein a gaseous oxygen product of desired purity and a cold nitrogen product are withdrawn, operating the first, high pressure rectification stage with a high liquid-vapor reflux ratio to produce a nitrogen rich liquid nearly devoid of oxygen and argon at the top of such first stage providing sufficient rectification steps in the second low pressure rectification stage to substantially complete oxygen and nitrogen separation and providing excess rectification steps at the top cold end of this second stage, introducing the very high purity nitrogen reflux liquid from said first stage into the top of said excess rectification steps of said second stage to establish an oxygen pinch condition over said excess rectification steps and utilize such reflux liquid principally to wash argon out of the rising vapor passing upwardly through these steps, regulating the purity of the nitrogen-rich reflux liquid by controlling the rate at which such liquid is transferred from said first to said second rectification, sensing the oxygen pinch condition by measuring the temperature difference across two rectification steps below one of the feed points to the second stage, withdrawing from a zone of the second rectification stage where the argon content is high, a fluid comprising mainly oxygen and argon to be further distilled in auxiliary rectification to produce an argon product and an oxygen product that is returned to the second rectification stage, and controlling said temperature difference across said two rectification steps by regulating the rate of net argon withdrawal from said second stage.

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**UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION**

Patent No. 2,934,908

May 3, 1960

Robert E. Latimer

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 53, for "flux" read -- reflux --.

Signed and sealed this 6th day of June 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents