April 3, 1951 G. E. SIMPSON 2,547,177

PROCESS OF AND APPARATUS FOR SEPARATING TERNARY GAS MIXTURES

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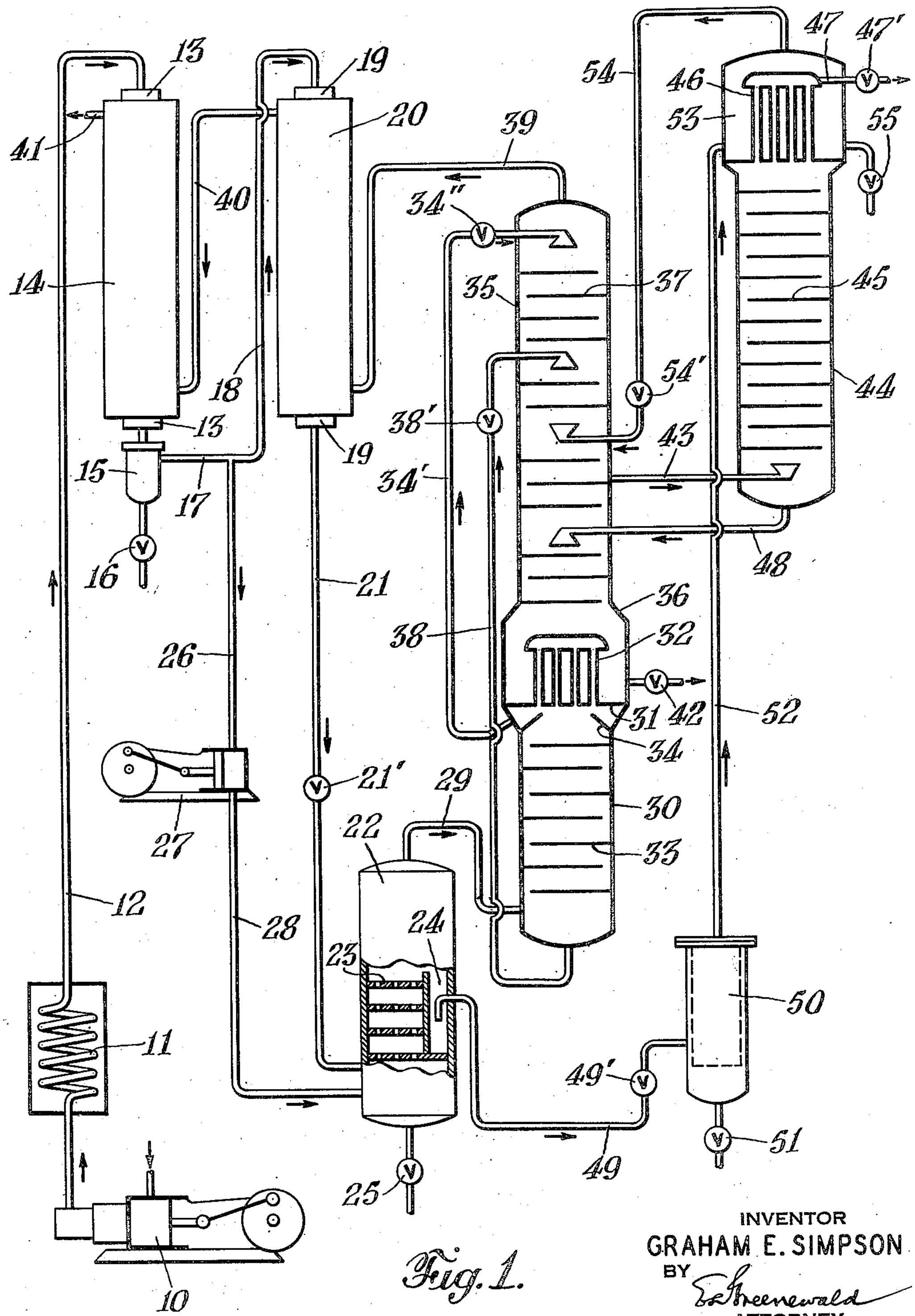

Fig. 1.

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April 3, 1951 | G. E. SIMPSON | 2,547,177

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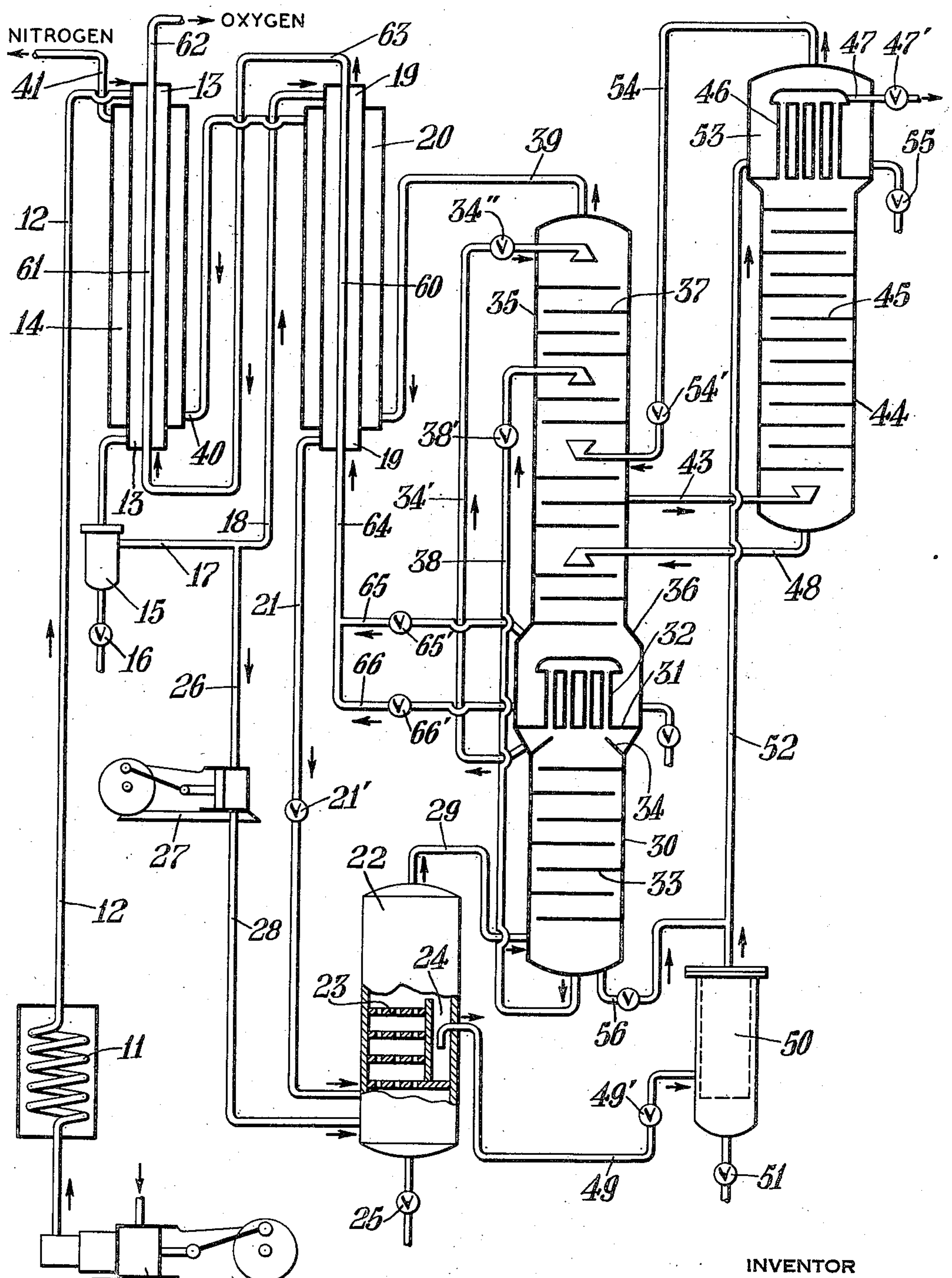

Fig. 2.

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PROCESS OF AND APPARATUS FOR SEPARATING TERNARY GAS MIXTURES

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11 Claims. (Cl. 62—175.5)

1

This invention relates to a process of and apparatus for separating ternary gas mixtures of relatively low boiling point into their constituents by low temperature rectification, and more particularly to the low temperature separation of air to provide oxygen, nitrogen, and argon products, with the simultaneous elimination of certain undesirable higher boiling point impurities which occur in the original gas mixture or air in very small proportions.

As set forth in United States Patent No. 2,287,158 of E. F. Yendall, the residual carbon dioxide and hydrocarbon impurities in air may be removed prior to low temperature rectification of air by scrubbing the air after it has been cooled to about its condensing temperature with a fraction of liquid air to entrain the impurities in the liquid air. The impurity-free air may be rectified, but the impurities must be removed from the liquid fraction. According to the aforementioned patent, the impurity removal is effected by evaporating a major part of the impurity-containing liquid by heat exchange with a gaseous oxygen product to make liquid oxygen. The concentrated residue of the evaporation is withdrawn and discarded. Other methods of effecting a heat exchange to evaporate and concentrate the impurity-charged scrubber liquid have been proposed, but in general such methods involve more or less loss of efficiency.

The recovery of an argon product when separating air by low temperature rectification has been accomplished by withdrawing vapor from a part of the final air rectification where the vapor has a substantial argon content, and then subjecting such withdrawn vapor to an auxiliary rectification. To provide reflux for such auxiliary rectification, various expedients have been proposed which generally incurred some losses resulting in increased power requirements.

It is a principal object of the present invention to provide an improved process of and apparatus for separating a ternary gas mixture such as air with the simultaneous elimination of impurities having higher boiling points than those of the components separated. Other objects of this invention are to provide a process of and apparatus for separating air to recover oxygen and argon with the simultaneous elimination of impurities collected in a liquid fraction of the air to be separated, in which the refrigeration produced by evaporation of the impurity-containing air may be usefully employed for supplying a reflux liquid for washing higher boiling components from an argon-rich vapor; and for integrating with the

2

main rectification of air an auxiliary rectification of argon-containing vapors and a preliminary separation from air to be rectified of higher boiling impurities in an economical manner, and which provides a system that is substantially self-regulating, easy to operate, and relatively simple to construct. A further object of the invention is to provide a method of and apparatus for separation of air by low temperature rectification including the elimination of impurities from air by concentrating them in a liquefied fraction of air in which a major part of the impurities which are entrained in a solid state in such liquefied fraction may be removed by filtration and the remainder of the impurities subsequently removed by distillation so that the amount of impurity-containing residue to be discarded is reduced to an immaterial amount.

These and other objects and advantages of this invention will become apparent from the following description and the accompanyng drawing in which:

Fig. 1 is a diagrammatic elevational view of an exemplary apparatus illustrating the principles of the invention; and

Fig. 2 is a similar view of an alternative system according to the invention for producing gaseous oxygen.

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 free of higher boiling 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 instead of liquid state and/or simultaneously obtain nitrogen in a high state of purity. Also it is contemplated that the argon-enriched vapor may be subjected to an additional auxiliary rectification if it is desired to obtain argon product of very high purity.

Referring now to the drawing and particularly to Fig. 1, the apparatus for preparing a gas mixture or air for rectification may be any of several known forms, that schematically illustrated being particularly suitable when the oxygen product is to be taken away in liquid form. A multi-stage compressor 10 compresses air to a relatively high pressure and such compressed air after being cooled in a water-cooled after-cooler 11 is passed through a conduit 12 to the inlet end of a compressed air passage 13 extending through a countercurrent heat exchanger 14. In the heat exchanger 14 the compressed air is cooled sufficiently to eliminate the moisture. Such moisture-removing heat exchangers are customarily provided in duplicate so that accumulated moisture can be removed from one of the heat exchangers while the other is in service. A trap 15 with a drain valve 16 may be mounted at the lower end of the passage 13.

From the trap 15 the compressed air flows through a conduit 17 having a branch 18 connected to the inlet end of a compressed air passage 19 extending through a liquefying heat exchanger 20. The cold liquefied air formed in the heat exchange passage 19 is conducted through a conduit 21 to a scrubber-separator chamber 22. The scrubber-separator chamber may be similar to that disclosed in the aforesaid United States Patent No. 2,287,158 and, as shown, comprises a chamber 22 within which are some perforated plates 23 or other means for effecting intimate mixing of gas and liquid. The conduit 21 enters below the plates 23 and there is provided an overflow cup 24 with its upper opening immediately above the upper plate 23. The scrubber-separator 22 may also be provided with a drain 25, the valve of which generally remains closed during operation.

A branch 26 of the conduit 17 conducts a substantial proportion of the compressed air to the inlet of an expansion engine 27. This engine expands the air passed therethrough with production of external work so that the expanded air has a temperature substantially corresponding to its condensing temperature at the pressure existing in the scrubber-separator, which is preferably about the same as the pressure of the first stage of rectification. This is of the order of 70 p. s. i. gauge. The expanded air is led by a conduit 28 from the expansion engine to the lower part of the scrubber-separator 22. Interposed in the conduit 21 is an expansion valve 21′ through which the liquefied portion of the compressed air is throttle expanded to the pressure of the scrubber-separator. The scrubber-separator 22 is preferably constructed with sufficient space above the gas and liquid contact means so that no drops of liquid are entrained in the vapor at the top of the scrubber-separator. The vapor, free of higher boiling point impurities, passes through a conduit 29 from the top of the scrubber-separator to the high-pressure stage or lower column 30 of a two-stage air rectifying apparatus.

This air rectifying apparatus, except as explained hereafter, is generally of customary construction. The lower column or high-pressure stage chamber 30 is closed at its upper end by a tube sheet 31 to which are connected the tubes of a condenser 32. The chamber 30 may contain customary column trays 33 such as perforated plates which effect intimate contact with vapors rising in the column and reflux liquid flowing down the column. Under the tube sheet 31 there is an annular shelf 34 for collecting liquid condensed by the outer tubes of the condenser 32. Such liquid that collects on the shelf 34 is substantially pure nitrogen.

The upper column or low-pressure rectifying chamber 35 extends above the tube sheet 31 and is formed at the lower end to provide a chamber 36 about the condenser 32 for effecting the boiling of liquid oxygen therein to produce vapors for the rectifying action in the upper column 35. The oxygen boils at the low pressure of the upper column at a temperature which is lower than the condensing temperature of nitrogen in the condenser 32 under the pressure of the lower

column. The nitrogen collected on the shelf 34 is transferred through a conduit 34′ provided with an expansion valve 34″ to the upper end of the upper column 35. This supplies reflux for the upper part of the upper column which is provided with the customary trays 37. Liquid that collects at the bottom of the lower column chamber 30 and which is richer in oxygen than air, is transferred by a conduit 38 controlled by an expansion valve 38′ to an intermediate point of the upper column 35.

The nitrogen product of rectification leaves the upper column 35 through a conduit 39 connected to the colder end of the heat exchanger 20 from which a conduit 40 conducts the effluent nitrogen to the cold end of heat exchanger 14. The nitrogen escapes from the heat exchanger 14 through an outlet 41 at substantially atmospheric temperature.

When the upper column is in regular operation and the liquid oxygen withdrawal at a valved outlet 42 from the chamber 36 is at a rate such that high-purity oxygen is produced, it is found that a substantial ratio of the argon of the original air is contained in the vapors at an intermediate point of the upper column. At such intermediate point a vapor outlet conduit 43 is connected to conduct the argon-containing vapor into the lower part of an auxiliary rectifying column 44. This column may also contain gas and liquid contact means such as trays 45. The argon-containing vapor passes upwardly through the column 44 in which it is washed with a reflux liquid produced by a condenser 46 at the top of the column 44. The vapors on passing through the tubes of condenser 46 are subjected to partial liquefaction, the liquid produced being rich in argon and forming a suitable reflux for the auxiliary column 44. The argon-rich vapor which is not condensed passes through the condenser 46 and is withdrawn through a conduit 47 provided with a control valve 47′. The liquid which eventually reaches the bottom of the column 44 is substantially stripped of its argon content and is mainly oxygen, and this liquid is preferably drained by a conduit 48 into the upper column 35 at a point below the vapor conduit 43.

The liquid that overflows into the cup 24 is withdrawn through a conduit 49 that conducts it to a filter 50. Preferably there is provided an expansion valve 49′ interposed in the conduit 49 so that the scrubber liquid may be expanded to a lower pressure before it is filtered and thereby its temperature will be reduced. The filter 50 is diagrammatically illustrated and usually is one of a duplicate set arranged so that one filter may be cleaned while another is in service. The filter is provided with a drain valve 51 for use when cleaning the filter. The filtered scrubber liquid is passed by a conduit 52 from the filter 50 to a chamber 53 surrounding the condenser 46 at the top of the auxiliary column. This scrubber liquid, due to the fact that it contains a large proportion of nitrogen, boils at a lower temperature than the condensing temperature of oxygen and therefore heat exchange readily occurs to effect partial condensation of the vapors passing through the condenser 46. The vaporized portion of the scrubber liquid passes through a conduit 54 into the upper column 35 so that these vapors, which are now free of higher boiling impurities, may also be rectified. The conduit 54 may also be provided with a regulating valve 54′.

Since a large part of the higher boiling impurities will be removed by the filter 50 and only a small amount will pass into the chamber **53**, most of the scrubber liquid that enters the chamber **53** may be vaporized and passed into the upper column **35**, and there will be only a very slow increase in the concentration of higher boiling point impurities in the liquid being evaporated in chamber **53**. In order that such concentrate may be removed, preferably at infrequent intervals, a drain valve **55** is provided, connected to a lower part of the chamber **53**.

It is believed that the operation of the apparatus is clear from the above description. It will be seen that the withdrawal of a vapor containing the constituent of intermediate volatility (for example, argon), washing down a major part of the higher boiling component (oxygen) from the withdrawn vapor and returning such liquid to the main rectification, makes it possible to obtain the higher boiling component from the chamber **36** in a high state of purity, the lower boiling component from the top of the main rectification in a high state of purity, and to recover a concentrate of the intermediate boiling component which, if desired, can be further purified or subjected to another rectification to eliminate residual low boiling component.

The undesired or dangerous impurities are effectively eliminated by concentrating them in a liquid from which they can be removed before they enter the rectification zones. In air separation the impurities are concentrated in a liquid of high nitrogen content. By filtering the main bulk of impurities from the scrubber liquid, a concentration of the very small remainder that may pass the filter in dissolved state may be effected by evaporation of practically all the filtered scrubber liquid and draining off only a very small residue without increasing the impurity concentration above dangerous limits. Effecting the vaporization of the scrubber liquid by heat exchange with vapor at the top of the auxiliary column provides efficient recovery of the refrigeration in the scrubber liquid.

When oxygen is withdrawn at **42** in the liquid state to make liquid oxygen product as in Fig. 1, the proportion of the air liquefied is correspondingly high so that an effective quantity of scrubber liquid is produced for both efficient scrubbing action and for refrigeration of the auxiliary column. If it is desired to make gaseous oxygen, the make oxygen could be withdrawn from the chamber **36** in either the liquid or gaseous states, as illustrated in Fig. 2. When the oxygen is withdrawn as liquid, it is heated countercurrently in the liquefying heat exchanger **20** by providing therethrough an oxygen passage **60** wherein the oxygen is vaporized to produce gaseous oxygen and the required amount of liquid air in passage **19**. If the oxygen is withdrawn from chamber **36** in gaseous state, the amount of liquid air entering the scrubber at **21** will be much smaller and it will be necessary to augment the scrubber liquid for efficient refrigeration of the condenser **46** at the top of the auxiliary column **44**. This can conveniently be accomplished by providing a valved by-pass connection **56** between the bottom of the chamber **30** and the conduit **52**.

In the embodiment of Fig. 2, the features similar to those already described in connection with Fig. 1 are designated by the same reference numbers. As previously mentioned in connection with Fig. 2, the heat exchanger **20** is additionally provided with a passage **60** for outgoing oxygen. Similarly the heat exchanger **14** is provided with an outgoing oxygen passage **61** which has an outlet **62** for the warm gaseous oxygen product. A conduit **63** connects the warm end of passage **60** with the cold end of passage **61**. The inlet **64** to the passage **60** is provided with a connection **65** to the vapor space of the chamber **36** and a connection **66** to the liquid space of chamber **36**. These connections are controlled by valves **65'** and **66'** respectively.

With valve **65'** closed, and valve **66'** adjusted, the liquid oxygen make withdrawn from chamber **36** through connection **66** is vaporized in heat exchanger passage **60** to liquefy air in the heat exchanger passage **19**. Obviously, due to the refrigeration thus recovered by such liquid oxygen evaporation, the refrigeration produced by compression and expansion may be less than in the case of Fig. 1. With valve **66'** closed and valve **65'** adjusted, gaseous oxygen is drawn from the chamber **36** and warmed in the passages **60** and **61**, and in such case the latent heat of vaporization of the make oxygen is supplied by the condenser **32** instead of by the air in heat exchanger passage **19** so that the scrubber liquid is augmented by liquid from the base of the chamber **30**.

Obviously, if desired, the refrigeration contained in the argon product may be recovered by passing it through special heat exchange passages which may be provided therefor through the heat exchangers **20** and **14**.

It will be seen that the systems described are efficient in that refrigeration contained in the scrubber liquid is returned. The auxiliary column is substantially self-regulating and the argon production is very simply controlled by regulating the withdrawal at valve **47'**. There is practically no interference between the adjustments for controlling the oxygen purity and recovery and those for the argon production and the removal of argon makes it easier to obtain high purity oxygen with good yield.

It is to be understood that changes in carrying out the above-described process and changes in the apparatus illustrated may be made without departing from the principles of the invention.

What is claimed is:

1. Process for separating air by low temperature rectification to obtain oxygen, argon, and nitrogen products which comprises compressing, cooling, and drying air to eliminate substantially all the moisture therefrom; further cooling and partially liquefying such air; scrubbing the cooled gaseous portion of the air with the liquefied portion to provide an impurity-free gaseous fraction and an impurity-containing liquid fraction; rectifying said impurity-free gaseous fraction to form an oxygen product of desired purity and a cold gaseous nitrogen product; withdrawing from a zone of the main rectification 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 from said auxiliary rectification; producing said reflux by a heat exchange between vapor of said auxiliary rectification and said impurity-containing liquid fraction to substantially vaporize said fraction and form an impurity-containing concentrate; removing said concentrate; passing the impurity-free vapors from said vaporization to the main rectification; withdrawing an argon concentrate from said auxiliary rectification; and utilizing at least the nitrogen product for countercurrently cooling incoming air.

2. A process for separating air according to claim 1 which includes the step of returning to said main rectification the used reflux liquid from said auxiliary rectification.

3. A process for separating air according to claim 1 which includes the step of subjecting the impurity-containing liquid fraction to filtration for the removal of solidified impurities prior to said heat exchange with the vapors of said auxiliary rectification.

4. A process for the separation of a gas mixture of three main components including also a minor amount of higher boiling point impurities which comprises providing such a mixture in conditions of pressure and temperature in which a major part of the mixture is at condensation temperature and a minor part is liquefied and intimately mixed with the major part; separating the major and minor parts so that the impurities are contained substantially all in the minor liquid part; rectifying the impurity-free major part to form a product of the higher boiling component of desired purity, a product comprising mainly the lowest boiling point component, and a vapor at an intermediate zone of the rectification including the intermediate boiling point component; withdrawing said vapor from the intermediate zone and subjecting it to an auxiliary rectification by washing with a reflux liquid formed by condensation of part of the vapor of said auxiliary rectification, withdrawing an intermediate boiling point component product from said partial condensation; effecting substantial vaporization of said minor liquid part by heat exchange with said vapor of the auxiliary rectification to form said reflux liquid and accumulate a remainder containing impurities; withdrawing such remainder to eliminate the impurities; and passing the vapor of said vaporization to the main rectification.

5. A process for separating a ternary gas mixture according to claim 4 which includes the step of subjecting the minor liquid part to filtration for removal of solidified impurities prior to said vaporization.

6. A process for separating a ternary gas mixture according to claim 5 which includes the step of returning to the main rectification a liquid remainder of the reflux liquid employed in the auxiliary rectification.

7. A process for the separation of a gas mixture of three main components including also a minor amount of higher boiling point impurities which comprises providing such a mixture in conditions of pressure and temperature in which a major part of the mixture is at condensation temperature and a minor part is liquefied and intimately mixed with the major part; separating the major and minor parts so that the impurities are contained substantially all in the minor liquid part; subjecting the impurity-free major part to a main rectification in two stages, the products of a first stage being passed to a second stage and the second stage forming a product of the higher boiling component of de-

sired purity, a product comprising mainly the lowest boiling point component, and a vapor at an intermediate zone of the rectification including the intermediate boiling point component; withdrawing said vapor from the intermediate zone and subjecting it to an auxiliary rectification by washing with a reflux liquid formed by condensation of part of the vapor of said auxiliary rectification, withdrawing an intermediate boiling point component product from said partial condensation; subjecting said minor portion to filtration to remove at least part of the impurities; then effecting substantial vaporization of said minor liquid part by heat exchange with said vapor of the auxiliary rectification to form said reflux liquid and accumulate a remainder containing impurities; withdrawing such remainder to eliminate the impurities; and passing the vapor of said vaporization to the main rectification.

8. A process for separating a ternary gas mixture according to claim 7 which includes the step of returning to the main rectification a liquid remainder of the reflux liquid employed in the auxiliary rectification.

9. Apparatus for the separation of a ternary gas mixture containing impurities which apparatus comprises means for providing a supply of such mixture in conditions of pressure and temperature in which a major part of the mixture is at condensation temperature and a minor part is liquefied and mixed with the major part; means for separating such supply into an impurity-free vapor fraction and a liquid fraction containing the impurities; a main rectifying column; means for passing the vapor fraction to the rectifying column for rectification therein; an auxiliary rectifying column having a reflux condenser and a boiler chamber around the condenser; means for passing vapor from an intermediate part of the main rectifying column to the lower part of the auxiliary column; means for passing said liquid fraction to said boiler chamber; means for passing vapor from the boiler chamber to said main column; and an impurity drain at a low part of the boiler chamber.

10. Apparatus according to claim 9 which includes means for draining reflux liquid from the bottom of the auxiliary column to said main column.

11. Apparatus according to claim 9 which includes a filter interposed in said means for passing the liquid fraction to the boiler.

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