

July 21, 1936.

R. LINDE

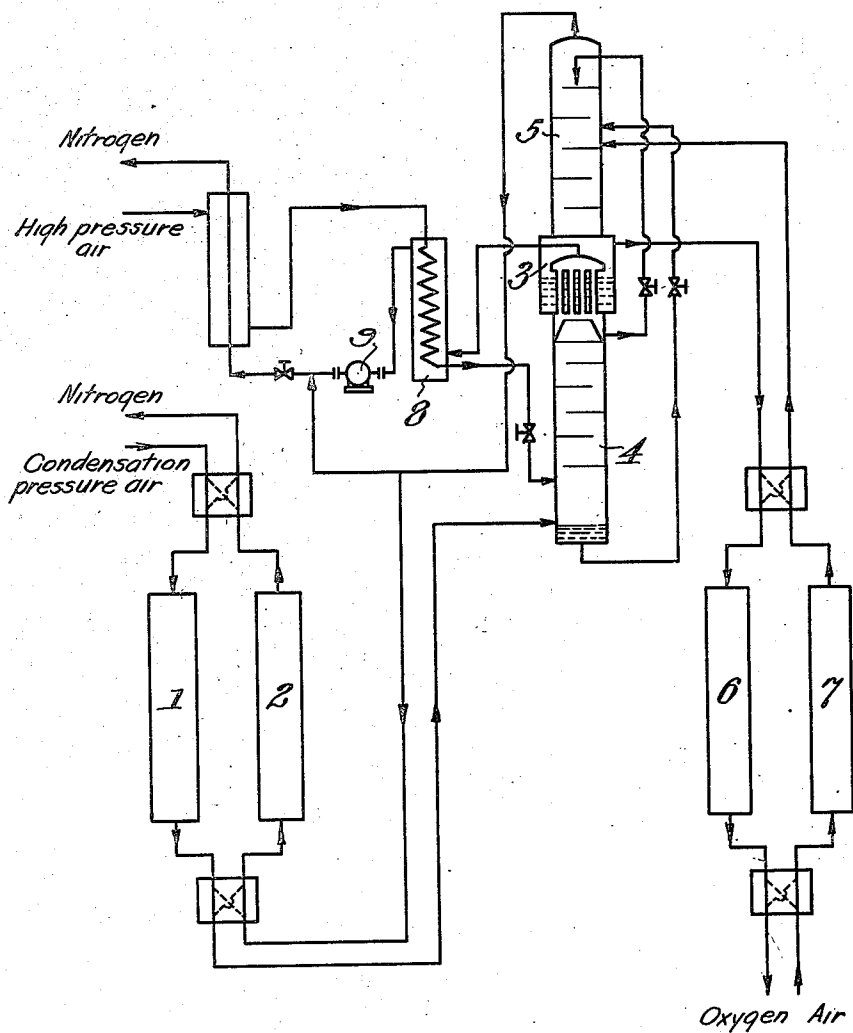
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PROCESS FOR SEPARATING LOW BOILING GAS MIXTURES

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3 Sheets-Sheet 1

Fig. 1.



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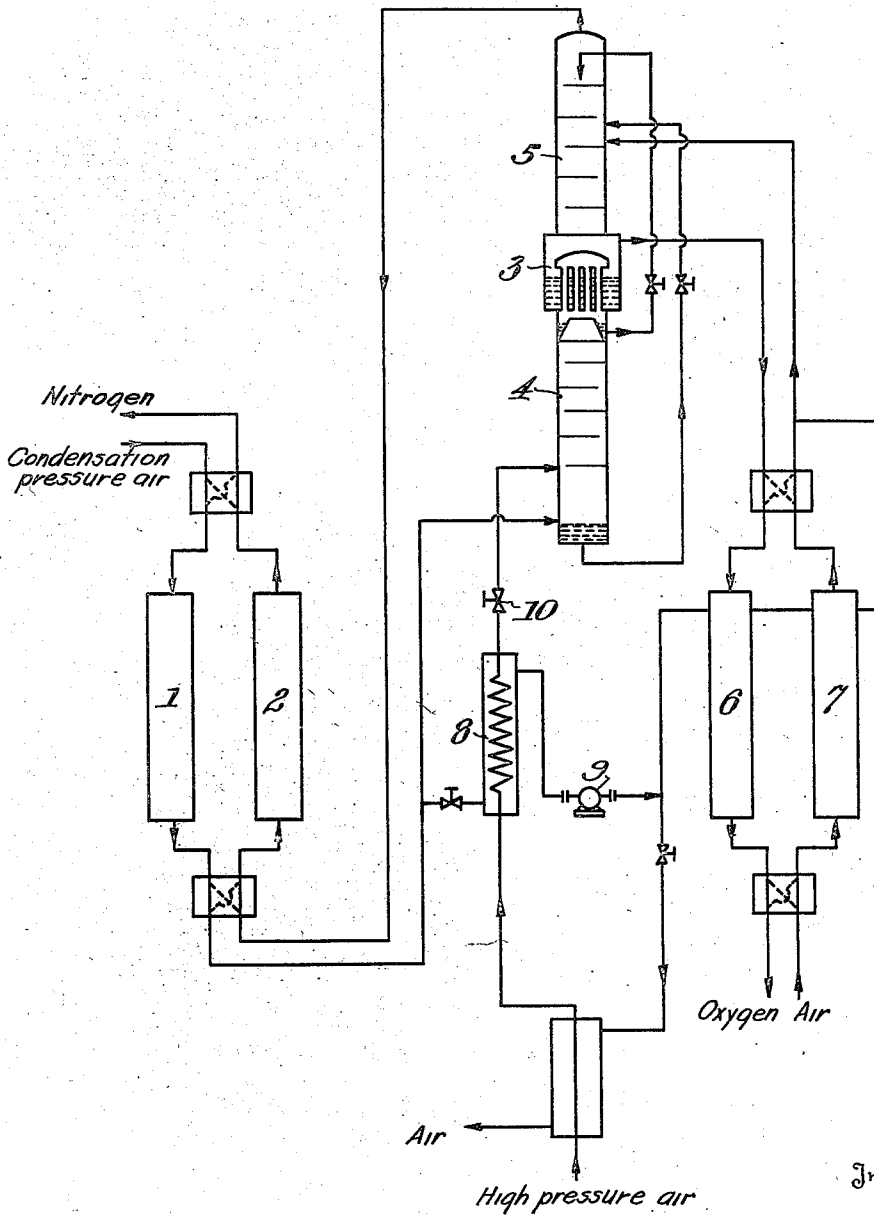
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Fig. 2.



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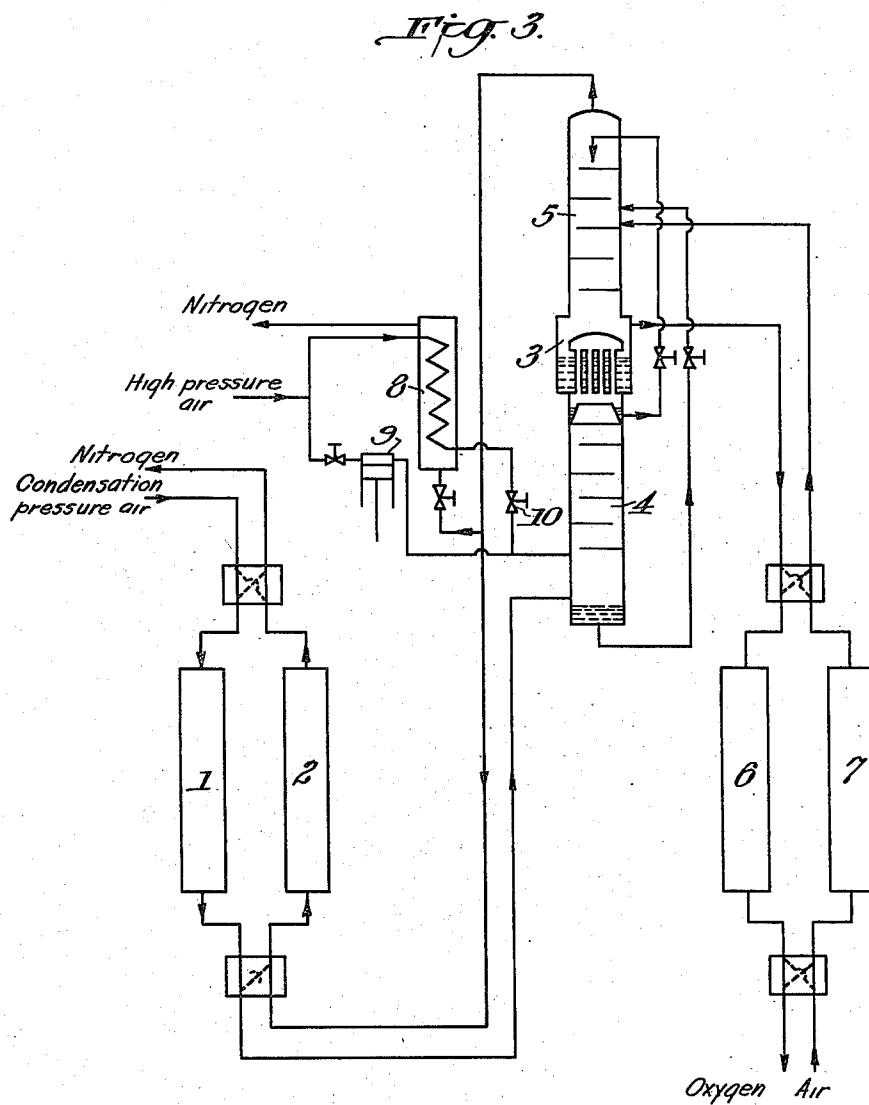
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3 Sheets-Sheet 3



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UNITED STATES PATENT OFFICE

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PROCESS FOR SEPARATING LOW BOILING
GAS MIXTURES

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11 Claims. (Cl. 62—175.5)

This invention relates to a process for separating low boiling gas mixtures, particularly adapted for separating air, the separation being performed in two stages, using periodically reversed cold regenerators, and compressing the air to be separated to such a pressure only which allows its liquefaction, or the liquefaction of the nitrogen, in heat exchange with boiling oxygen. In these so-called low pressure processes the cold necessary for compensating the losses was till now obtained by expanding in an expansion motor or a turbine a portion of the compressed air, or of the nitrogen separated under pressure, at low temperature. The rectification process in this method, however, is too closely coupled with the process of producing the cold required; for the quantity of the cold to be produced determines the quantity of gas which for the purpose of expansion, must be taken from the pressure column and which hereby is lost as a washing liquid for the upper column. As the separation plant must be regulated in such a way that the losses of cold varying according to the surrounding temperature, to the amount of liquid oxygen to be taken off and to other circumstances, are always exactly compensated, the rectification conditions will be favourable in exceptional cases only while in most cases the rectification will furnish either a poor output caused by a lack of washing liquid, or a surplus of washing liquid cannot be utilized.

It is the object of the present invention to provide a method for avoiding this difficulty and furthermore to reduce the amount of energy required for the separation. According to the invention a separate cold producing process by means of expanding a relatively small quantity of air compressed to high pressure is provided in order to compensate the variable portion of the losses, and, besides, an optional portion of the constant losses. The remaining amount of cold necessary to maintain the refrigeration balance is produced by expanding a certain quantity of nitrogen which, independent of the total amount of the cold required, may be kept absolutely constant in normal operation. Before expansion the nitrogen must be heated so far that no condensation takes place when expanded. Instead of using for this purpose a small quantity of air compressed to 10–20 atms. the air is compressed to a higher pressure of about 200 atms., and this high pressure air is used for producing cold by expanding it to atmospheric pressure.

This method of producing cold is particularly

advantageous as the further compression from 10 or 20 atms. to 200 atms. does not require much energy. If the ratio of air which is used for heating the nitrogen, amounts to 5% it is possible—even with simple throttling of the high pressure air—to produce 1 Kcal at low temperature with an additional expenditure of energy of about 0.01 H. P. only. The additional quantity of cold is large enough to allow relatively large quantities of oxygen to be withdrawn, if required, in liquid condition from the apparatus, a fact sometimes necessary if an enrichment of impurities in the evaporator shall be prevented. The fact that the expansion motor is nevertheless driven with constant power and a constant number of revolutions allows the expansion energy to be used in a much better way. While hitherto it was necessary to consume the energy of the expansion motor in a machine which—like a water pump—was able to follow the variations in power and speed of the expansion motor, or simply electrically to waste the expansion energy it is now possible to couple the expansion motor directly with a compressor for instance.

A modification of the method consists in replacing the nitrogen, taken from the pressure column and to be sent into the expansion motor, by a portion of the unseparated air under condensation pressure; after expansion this air is introduced into the second rectification column.

The quantity of nitrogen or low pressure air to be expanded in the expansion motor may, as mentioned above, be reduced to any desired degree while the lacking amount of cold is furnished by expanding high pressure air of due quantity and pressure. The limit to which the quantity of nitrogen may be reduced is zero, i. e. that the total refrigeration is produced by expansion of the high pressure air. The whole quantity of nitrogen thus becomes available as a washing liquid for the upper column offering, in consequence, the most favorable conditions for obtaining the best output and the highest purity of the separation products. It is of special advantage in this case to throttle only one portion of the high pressure air while expanding the rest with external work; hereby the efficiency of cold production is practically as favourable as before.

The production of cold may be performed, according to the well-known Heylandt process, by introducing the air into the expansion motor at a pressure of 200 atms. and ordinary temperature. Though the Heylandt process is known to

be one of the most economic processes for producing cold it was hitherto not possible to use this process in connection with gas separating processes (if no liquid oxygen or other liquid products are to be produced), for it is not possible totally to transmit the cold produced in the expansion motor to fresh air. Either the heat exchange is imperfect, and thus directly cold is lost, or the ratio of high pressure air passing through the expansion motor must be reduced which means an indirect loss of cold. Besides, in consequence of the small differences of temperatures, particularly large exchangers for heat transmission are necessary.

These disadvantages of the liquefaction process are now—according to the present invention—converted into a special advantage by using regenerators for the heat exchange. When employing regenerators it has practically proved necessary to withdraw a greater quantity of cold gas through the regenerators than hot gas is introduced in order to keep, by this addition of cold, the difference of temperature between hot and cold period in the cold part of the regenerators so small that the revaporization of the condensates separated from the fresh gas is absolutely guaranteed. The additional requirement of cold, necessary for this purpose, is now supplied in a particularly favourable manner by the cold excess of the said liquefaction process which otherwise could not be used.

Similar circumstances prevail with other methods of liquefaction in which a portion of the air is expanded with external work while the rest is throttled. Instead of using the Heylandt process it is possible e. g. to compress the greater portion of the air used for producing cold to 16 atms., precool it to about -40°C ., and expand it in an expansion motor while the rest of the air is compressed to about 40 atms., precooled to -40°C ., further cooled by the exhaust of the expansion motor, and then is throttled.

The larger quantity of washing liquid available in the upper column may be utilized, according to the present invention, by additionally blowing air into this column which air must be compressed to some tenths of one atmosphere above atmospheric only. This means a considerable economy in compression energy.

It may seem to be a disadvantageous complication to use air under three different pressures, particularly when using cold regenerators as the difficulties of correctly distributing the quantities of air to the regenerators become the greater the more currents of gas, i. e. the more regenerators, are required. This complication, however, may be avoided if, according to this invention, the quantity of air being blown into the upper column is chosen exactly as great regarding the heat contents, or—what is practically the same—the volume as the quantity of the oxygen obtained. In this case the usually necessary two pairs of regenerators are sufficient, the one of which provides for the heat exchange between nitrogen and the air at condensation pressure while the other pair provides for the heat exchange between oxygen and blast air. Of course, the cooling down of the small portion of air compressed to high pressure is separately effected in continually acting counter-current heat exchangers.

The invention will be more particularly described with reference to the accompanying drawings, in which:

Fig. 1 is a diagrammatic illustration of one embodiment of the invention; and

Figs. 2 and 3 are diagrammatic illustrations of modified embodiments of the invention.

The following example of producing oxygen of 65% purity out of 10,000 cu. metres of air per hour will illustrate one of the different ways in which the invention may be performed:—

7,000 cu. metres of the air to be separated are compressed to condensation pressure, i. e. about 14 atms., cooled to about condensation temperature in regenerators 1 or 2 of Fig. 1 in heat exchange with the separated nitrogen, then introduced into the pressure column 4 of a two-stage separation apparatus 3, and there separated in the known and usual way. (If the condensation of the air is performed in a reflux condenser and the liquid oxygen is vaporized while its vapors flow in the same direction as the liquid does, the condensation pressure may be lowered to about 3.2 atms.) About 1,350 cu. metres per hour of nitrogen, equal to about 20% of the treated air, are gaseously taken from the pressure column 4, or from the reflux condenser, and expanded with external work in the turbine 9 while the rest is used in liquid form in the upper column 5 as a washing liquid. 3,000 cu. metres of air per hour—just as much as oxygen is obtained—are compressed to 0.4 atms. only in a blast, cooled down in heat exchange with the oxygen in regenerators 6 or 7 to about condensation temperature, and then gaseously blown into the upper column 5.

To balance the cold losses about 500 cu. metres of air per hour are compressed to a pressure of 200 atms., cooled in counter-current heat exchange with the separation products, and suitably brought into heat exchange with the nitrogen in countercurrent heat exchanger 8 before it enters the expansion motor 9. Then the cold high pressure air is throttled, and—as desired—introduced into the first separation stage 4 as shown in Fig. 1 or into the second stage. For increasing the amount of refrigeration the high pressure air may be precooled to about -40°C . before the heat exchange with the separation products by means of a special refrigerating machine.

Fig. 2 of the drawings illustrates the method of operation referred to above in which the nitrogen taken from the pressure column to be sent into the expansion motor is replaced by a portion of the unseparated air under condensation pressure.

The air compressed to condensation pressure is cooled to condensation temperature in regenerators 1 or 2 in heat exchange with the separated nitrogen. A part of this air is warmed up in counter-current heat exchanger 8 in heat exchange with high pressure air to such an extent that upon expansion in turbine 9 no condensation takes place. After expansion it is mixed with low pressure air which has been cooled in regenerators 6 or 7 in heat exchange with the separated oxygen. The rest of the air compressed to condensation pressure, together with the high pressure air which has been throttled in valve 10, is introduced into pressure column 4 of the two-stage separation apparatus. The whole amount of nitrogen which is separated from the air in pressure column 4 is liquefied in condenser 3 and used as washing liquid in column 5, into which the remainder of the air to be separated, which has been compressed only slightly above atmospheric pressure, is blown in gaseous

condition together with the expanded air from the turbine.

Various changes may be made in the details of operation without departing from the invention or sacrificing any of the advantages thereof. For instance the ratio of nitrogen expanded in the expansion motor may be reduced, as described, to any optional value down to zero then producing the total amount of cold required by one of the high pressure methods mentioned before. This method of operation will be more particularly described with reference to Fig. 3. The air compressed to condensation pressure is cooled to condensation temperature in regenerator 1 or 2 in heat exchange with the separated nitrogen and introduced into column 4 of the two-stage separation apparatus 3. An amount of air equal to the amount of oxygen obtained is cooled under slight pressure in heat exchange with the oxygen in regenerators 6 and 7, and blown into rectification column 5 in gaseous form. The generation of cold is effected in this method of operation by expanding a portion of the air compressed to 200 atmospheres in the expansion engine 9, while the remainder, after precooling with nitrogen in countercurrent heat exchanger 8, is throttled in valve 10 and introduced into column 4. The precooling of the second portion of the high pressure air in countercurrent heat exchanger 8 can also be effected by heat exchange with the exhaust of the expansion engine 9. Instead of nitrogen a portion of the air compressed to condensation pressure may be expanded in the expansion motor. The quantity of air compressed to high pressure and the height of the pressure may vary according to the amount of cold actually required at any time.

As to the upper limit of nitrogen to be withdrawn from the first separation stage it should not exceed about 20% of the treated air when pure oxygen is to be produced. Though the usual calculation shows that it should be possible to withdraw much larger a quantity of nitrogen gaseously from the pressure column without diminishing the output it was found out, however, that in fact the output decreases rapidly when the above mentioned limit is surpassed, a fact probably due to the presence of argon which component prevails in the lower part of the rectification column, and renders the separation of oxygen much more difficult than it would be with nitrogen only present.

As the quantity of injecting air is automatically adjusted to the purity of the oxygen the process has a great adaptiveness, so that it becomes possible, in spite of the blowing in of air which renders the rectification more difficult, to produce oxygen of any desired degree of purity, even surpassing 99%. With decreasing purity of the oxygen a larger quantity of air may be introduced practically without compression. By this fact the energy required for the separation is additionally lowered besides the lowering due to the lowering of condensation pressure. Another advantage of the invention is the fact that the losses of compressed gas become smaller at each reversing of the regenerators as the pressure of the air passing through the oxygen regenerators is very low. In consequence the oxygen is less contaminated by the air remaining in the regenerators at reversal than it was till now, so that the oxygen is obtained in a higher degree of purity.

The process has been described for the example

of separating air into oxygen and nitrogen. In the same manner it may be used for separating other low boiling gas mixtures into two components. The lower boiling component then takes the place of nitrogen while the higher boiling one takes that of oxygen.

I claim:—

1. Process for separating a gas mixture, such as air, in a two-stage rectifying plant which comprises compressing the major portion of the air to such a pressure that the nitrogen separated under that pressure can be liquefied in heat exchange with the oxygen vaporizing in the bottom of the second stage of rectification, cooling said major portion of the air down to condensation temperature in periodically reversed cold regenerators in heat exchange with the separated gases, introducing the cooled air into the first stage of rectification, producing the cold required by compressing a minor portion of the air to high pressure; cooling at least a portion of said high pressure air by counter-current heat exchange with a compressed gas expanded with external work, throttling the cooled high pressure air, introducing the throttled air into one of the stages of rectification and completing the separation of the air into nitrogen and oxygen of desired purity in the second stage of rectification.

2. Process for separating a gas mixture, such as air, in a two-stage rectification plant, which comprises compressing the major portion of the air to such a pressure that the nitrogen separated under that pressure can be liquefied in heat exchange with the oxygen vaporizing in the bottom of the second stage of rectification, cooling said major portion of the air down to condensation temperature in periodically reversed cold regenerators in heat exchange with the separated gases, introducing the cooled air into the first stage of rectification, withdrawing from the first stage of rectification a constant quantity of the separated nitrogen, heating it, in heat exchange with a minor portion of the air, which has been compressed to high pressure and pre-cooled, to such an extent that no condensation takes place upon expanding it with external work, expanding the nitrogen, throttling the high pressure air, introducing the throttled air into one of the stages of rectification and completing the separation of the air into nitrogen and oxygen of desired purity in the second stage of rectification.

3. Process for separating a gas mixture, such as air, in a two-stage rectification plant, which comprises compressing the major portion of the air to such a pressure that the nitrogen separated under that pressure can be liquefied in heat exchange with the oxygen vaporizing in the bottom of the second stage of rectification, cooling said major portion of the air down to condensation temperature in periodically reversed cold regenerators in heat exchange with the separated gases, introducing most of said major portion of the air into the first stage of rectification, heating the rest of said major portion of the air in heat exchange with a minor portion of the air, which has been compressed to high pressure and pre-cooled, to such an extent that no condensation takes place upon expanding it with external work, expanding the rest of said major portion of the air and blowing it in gaseous form into the second stage of rectification, throttling the high pressure air, introducing the throttled air into one of the stages of rectification and completing the separation of the air into nitrogen and oxygen

of desired purity in the second stage of rectification.

4. Process for separating a gas mixture, such as air, in a two-stage rectification plant, which comprises compressing the major portion of the air to such a pressure that the nitrogen separated under that pressure can be liquefied in heat exchange with the oxygen vaporizing in the bottom of the second stage of rectification, compressing a further portion of the air only to a small pressure above atmospheric, cooling both said portions of the air down to condensation temperature in periodically reversed cold regenerators in heat exchange with the separated gases, introducing said major portion of the air into the first stage of rectification, blowing said further portion of the air in gaseous form into the second stage of rectification, withdrawing from the first stage of rectification a constant quantity of the separated nitrogen, heating it in heat exchange with a minor portion of the air, which has been compressed to high pressure and precooled, to such an extent that no condensation takes place upon expanding it with external work, expanding the nitrogen, throttling the high pressure air, introducing the throttled air into one of the stages of rectification, and completing the separation of the air into nitrogen and oxygen of desired purity in the second stage of rectification.

5. Process for separating a gas mixture, such as air, in a two-stage rectification plant, which comprises compressing the major portion of the air to such a pressure that the nitrogen separated under that pressure can be liquefied in heat exchange with the oxygen evaporating in the bottom of the second stage of rectification, compressing a further portion of the air only to a small pressure above atmospheric, cooling both said portions of the air down to condensation temperature in periodically reversed cold regenerators in heat exchange with the separated gases, introducing most of said major portion of the air into the first stage of rectification, heating the rest of said major portion of the air in heat exchange with a minor portion of the air, which has been compressed to high pressure and precooled, to such an extent that no condensation takes place upon expanding it with external work, expanding it, blowing the expanded air together with said further portion of the air in gaseous form into the second stage of rectification, throttling the high pressure air, introducing the throttled air into one of the stages of rectification, and completing the separation of the air into nitrogen and oxygen of desired purity in the second stage of rectification.

6. Process for separating a gas mixture, such as air, in a two-stage rectification plant, which comprises compressing the major portion of the air to such a pressure that the nitrogen separated under that pressure can be liquefied in heat exchange with the oxygen vaporizing in the bottom of the second stage of rectification, compressing a further portion of the air equal in amount to the oxygen separated only to a small pressure above atmospheric, cooling both said portions of the air down to condensation temperature in periodically reversed cold regenerators in heat exchange with the separated gases, introducing said major portion of the air into the first stage of rectification, blowing said further portion of the air in gaseous form into the second stage of rectification, withdrawing from the first stage of recti-

fication a constant quantity of the separated nitrogen, heating it in heat exchange with a minor portion of the air, which has been compressed to high pressure and precooled, to such an extent that no condensation takes place upon expanding it with external work, expanding the nitrogen, throttling the high pressure air, introducing the throttled air into one of the stages of rectification, and completing the separation of the air into nitrogen and oxygen of desired purity in the second stage of rectification.

7. Process for separating a gas mixture, such as air, in a two-stage rectification plant, which comprises compressing the major portion of the air to such a pressure that the nitrogen separated under that pressure can be liquefied in heat exchange with the oxygen evaporating in the bottom of the second stage of rectification, compressing a further portion of the air equal in amount to the oxygen separated only to a small pressure above atmospheric, cooling both said portions of the air down to condensation temperature in periodically reversed cold regenerators in heat exchange with the separated gases, introducing most of said major portion of the air into the first stage of rectification, heating the rest of said major portion of the air in heat exchange with a minor portion of the air, which has been compressed to high pressure and precooled, to such an extent that no condensation takes place upon expanding it with external work, expanding it, blowing the expanded air together with said further portion of the air in gaseous form into the second stage of rectification, throttling the high pressure air, introducing the throttled air into one of the stages of rectification, and completing the separation of the air into nitrogen and oxygen of desired purity in the second stage of rectification.

8. Process for separating a gas mixture, such as air, in a two-stage rectification plant, which comprises compressing the major portion of the air to such a pressure that the nitrogen separated under that pressure can be liquefied in heat exchange with the oxygen vaporizing in the bottom of the second stage of rectification, cooling said major portion of the air down to condensation temperature in periodically reversed cold regenerators in heat exchange with the separated gases, introducing the cooled air into the first stage of rectification, producing the cold required by compressing a minor portion of the air to high pressure, expanding a part of said high pressure air with external work, cooling the rest of said high pressure air in heat exchange with the expanded portion, throttling the cooled portion, introducing the throttled air into one of the stages of rectification, and completing the separation of the air into nitrogen and oxygen of desired purity in the second stage of rectification.

9. Process for separating a gas mixture, such as air, in a two-stage rectification plant, which comprises compressing the major portion of the air to such a pressure that the nitrogen separated under that pressure can be liquefied in heat exchange with the oxygen vaporizing in the bottom of the second stage of rectification, cooling said major portion of the air down to condensation temperature in periodically reversed cold regenerators in heat exchange with the separated gases, introducing the cooled air into the first stage of rectification, producing the cold required by compressing a minor portion of the air to high pressure, expanding a part of said high pressure air with external work, cooling the rest of said high

pressure air in heat exchange with the separated gases, throttling the cooled portion, introducing the throttled air together with the expanded air into one of the stages of rectification, and completing the separation of the air into nitrogen and oxygen of desired purity in the second stage of rectification.

10. Process for separating a gas mixture, such as air, in a two-stage rectification plant, which comprises compressing the major portion of the air to such a pressure that the nitrogen separated under that pressure can be liquefied in heat exchange with the oxygen vaporizing in the bottom of the second stage of rectification, compressing a further portion of the air only to a small pressure above atmospheric, cooling both said portions of the air down to condensation temperature in periodically reversed cold regenerators in heat exchange with the separated gases, introducing said major portion of the air into the first stage of rectification, blowing said further portion of the air in gaseous form into the second stage of rectification, producing the cold required by compressing a minor portion of the air to high pressure, expanding a part of said high pressure air with external work, cooling the rest of said high pressure air in heat exchange with the expanded portion, throttling the cooled portion, introducing the throttled air into one of the stages of rectification, and completing the separation of the air

into nitrogen and oxygen of desired purity in the second stage of rectification.

11. Process for separating a gas mixture, such as air, in a two-stage rectification plant, which comprises compressing the major portion of the air to such a pressure that the nitrogen separated under that pressure can be liquefied in heat exchange with the oxygen vaporizing in the bottom of the second stage of rectification, compressing a further portion of the air only to a small pressure above atmospheric, cooling both said portions of the air down to condensation temperature in periodically reversed cold regenerators in heat exchange with the separated gases, introducing said major portion of the air into the first stage of rectification, blowing said further portion of the air in gaseous form into the second stage of rectification, producing the cold required by compressing a minor portion of the air to high pressure, expanding a part of said high pressure air with external work, cooling the rest of said high pressure air in heat exchange with the separated gases, throttling the cooled portion, introducing the throttled air together with the expanded air into one of the stages of rectification, and completing the separation of the air into nitrogen and oxygen of desired purity in the second stage of rectification.

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