G. CLAUDE.

METHOD OF SEPARATING THE CONSTITUENTS OF GASEOUS MIXTURES.

APPLICATION FILED DEC. 6, 1917.

1,426,461. Patented Aug. 22, 1922.

Fig. 1.

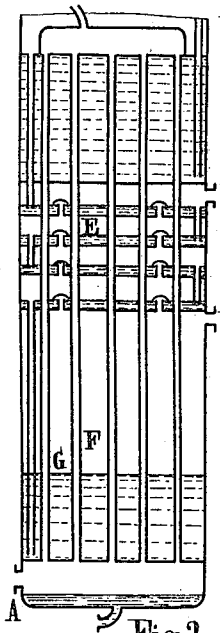


Fig. 2.

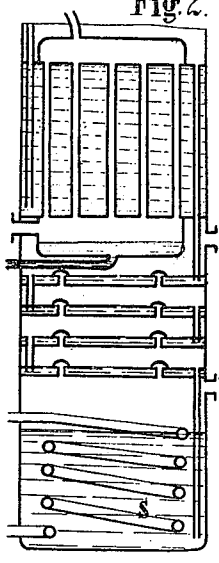
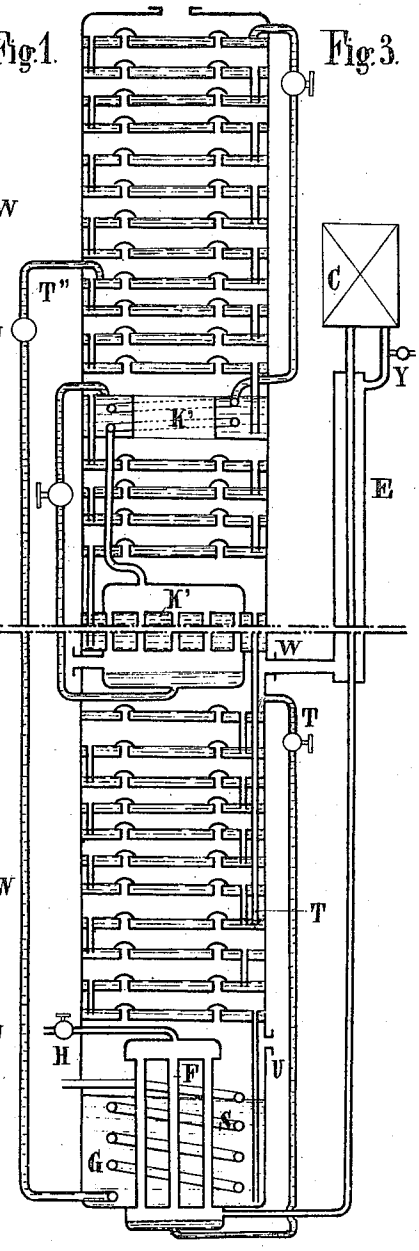


Fig. 3.



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UNITED STATES PATENT OFFICE.

GEORGES CLAUDE, OF BOULOGNE-SUR-SEINE, FRANCE, ASSIGNOR TO L'AIR LIQUIDE SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE, OF PARIS, FRANCE.

METHOD OF SEPARATING THE CONSTITUENTS OF GASEOUS MIXTURES.

1,426,461. Specification of Letters Patent. Patented Aug. 22, 1922.

Application filed December 6, 1917. Serial No. 205,708.

To all whom it may concern:

Be it known that I, GEORGES CLAUDE, a citizen of the Republic of France, residing at Boulogne-sur-Seine, 14 Boulevard d'Auteuil, France, have invented a new and useful Method of Separating the Constituents of Gaseous Mixtures, which is fully set forth in the following specification.

This invention relates to the separation of the constituents of gaseous mixtures liquefying at low temperatures, and has for its object the recovery of such constituents in condition of commercial purity in an economical and efficient manner.

While the invention is described more particularly with respect to the separation of the constituents of the atmosphere, the method is obviously applicable to other gaseous mixtures having similar physical characteristics, and the description is, therefore, by way of illustration of the invention.

In the ordinary apparatus for the production of oxygen and nitrogen from atmospheric air by liquefaction and rectification, it is known that the liquid oxygen which arrives in the part underneath of the rectifying column, and which is called the vaporiser, is there vaporised by means of the compressed air, to be treated, which thereby becomes liquefied. Of the liquid thus vaporised about four fifths rises in the rectifying column for the purpose of progressively transforming the liquids that flow downward therein into liquid oxygen, which, arriving at the vaporiser, replaces the vaporised oxygen. The remaining fifth, corresponding to the quantity of oxygen contained in the air treated is withdrawn directly from the vaporiser and constitutes one of the products of the manufacture. The gases which ascend in the rectifying column in contact with the descending liquids are thereby progressively transformed into gas rich in nitrogen which escapes at the upper part of the column.

However, in consequence of the presence of argon in the atmospheric air, the operation does not proceed with this simplicity in actual practice. The argon, the boiling point of which is very near that of oxygen, separates therefrom with great difficulty, and in order to obtain very pure oxygen, which is being sought for more and more in industry, it is necessary to let the greatest part of the argon escape with the nitrogen, thereby carrying away with it a part of the oxygen. There is, therefore, both a loss of the output in oxygen and a diminution in the purity of the nitrogen.

In a prior United States Patent No. 1,068,219, I have described a means of obviating the latter defect without impairing the purity of the nitrogen. This means consists in letting the not quite pure liquid oxygen obtained in the vaporiser, be divided by an additional rectification into a small part of oxygen gas carrying with it practically the whole of the argon and of the remaining nitrogen and into a main portion formed of almost pure oxygen. But, since a part of the oxygen escapes with nitrogen and argon, this means gives only a greater purity of the oxygen and of the nitrogen but does not remove the disadvantage pointed above of a loss in the output of the oxygen.

The method which forms the present invention completes the above means by treating the above gaseous mixture rich in argon but charged with nitrogen and oxygen in such a way as to retain the oxygen of this mixture; it separates the impure liquid oxygen of the vaporiser into a first portion constituted by almost pure oxygen, a second portion containing the greater part or substantially all of the nitrogen, and a third portion composed of argon with very little oxygen and nitrogen.

To this effect the liquid oxygen from the usual rectifying column and which contains nearly the whole of the argon of the treated air with little nitrogen is introduced into an auxiliary cycle of liquefaction and rectification in which a certain quantity of a gas very rich in argon is treated in a closed circuit. This gas is compressed and liquefied and the resulting liquid serves to rectify in an auxiliary column the vapors evolved from the above impure liquid oxygen. The combined liquids during this rectification are transformed into very pure oxygen, whereas the argon, which constitutes the main impurity of the impure

liquid oxygen treated, escapes with very little oxygen at the upper part of this auxiliary column in the gaseous state together with the argon of the auxiliary cycle. As to the nitrogen also contained in the impure liquid oxygen treated, it will escape with this argon gas too; but the volume of the gas rich in argon traveling in the closed circuit is large enough so that the small portion of nitrogen which was contained in the impure liquid oxygen treated forms only a slight impurity which is further reduced as hereinafter described. Of this mixture of argon with little oxygen and nitrogen, a quantity corresponding to the quantity of argon carried by the impure liquid oxygen is withdrawn to constitute one of the products of the operation; the remainder of this mixture which is not withdrawn is further treated in the closed circuit; it is compressed, and liquefied with backward return, so as to give on the one part the liquid rich in argon which is used again as above in the auxiliary column, thus closing the circuit, and on the other part a residue which contains the greater part or substantially all of the nitrogen and which is withdrawn from the circuit, thus preventing its accumulation in the circuit.

In order to charge this closed circuit with the necessary auxiliary volume of gas, use is made, at the time this circuit is set into operation, of the gases evolved by the impure liquid oxygen withdrawn from the main rectifying column; these gases are compressed, liquefied and rectified in the above closed circuit, and are thereby progressively converted into the necessary gas rich by argon in virtue of the known self purification process by means of which a gaseous mixture liquefied and rectified over and over again, becomes richer and richer in its more volatile element when the gases are rectified by the liquids resulting from a previous reliquefaction. Of course, during this starting of the circuit no argon gas will be withdrawn as a product of manufacture; this withdrawal will only be possible when the desired purity is obtained.

The accompanying drawings will more fully illustrate the object of the invention.

Figure 1 is a reproduction of one of the figures of my earlier Patent No. 1,068,219 above referred to, and is given here in order to facilitate an understanding of the following description;

Figure 2 shows another form of the apparatus illustrated in Figure 1; and

Figure 3 shows a form of apparatus devised for carrying into effect the process in accordance with the present invention.

It will be understood that Figures 1 and 2 both illustrate the part underneath a known rectifying column for separating air into oxygen and nitrogen, that is to say, the vaporiser in which there collects the liquid impure oxygen that flows from the lower part of the rectifying column, and they illustrate also the additional rectifying column above first spoken of with reference to Patent No. 1,068,219.

In Figure 1, G is the vaporiser filled with impure liquid oxygen and comprising a nest of tubes F in the inside of which air is liquefied, E are the plates of this additional column, W is the exit of the mixture of argon and nitrogen with little oxygen, U is the exit for almost pure oxygen. It will be seen that since argon and little oxygen and nitrogen escape through W, these gases will not injure the purity of the nitrogen escaping at the top of the main rectifying column. According to the views expressed in this prior Patent No. 1,068,219, any system in which the compressed air to be treated is liquefied by indirect contact with the liquid oxygen to be evaporated may be employed, and a coil S may, for instance, be used for vaporizing the oxygen as illustrated by Figure 2.

Now referring to Figure 3, the upper part shows one form of an ordinary rectifying column with two vaporisers K, K′; the part underneath the vaporiser K is the one illustrating the present invention. In the first part, compressed air cooled in temperature exchangers, not shown, is admitted into the tubes of the vaporiser K and the liquid formed is introduced above the vaporiser K′. The portion of air not liquefied inside K is liquefied inside K′. Another part of the compressed cooled air is liquefied inside the coil S as will be shown afterwards, and the liquid collected is introduced by the pipe T″ into another part of the main rectifying column. In this column the air is thus separated in the known manner into gas rich in nitrogen escaping at its upper part, and into a liquid, rich in oxygen but still containing argon and some nitrogen which is collected outside the tubes of the vaporiser K.

This impure liquid oxygen is discharged through T, from the main rectifying column to the lower plates of an auxiliary rectifying column and flows from plate to plate in a direction opposite to that of the ascending gases, becoming richer in oxygen. Its admission into the lower vaporiser G is compensated for by the liquefaction in coil S of an equivalent quantity of compressed air, and the liquid formed inside S is sent by T″ into the main column as seen above.

The gases that escape from the top of the auxiliary column at W are compressed at C after passing through a temperature exchanger E, and after passing through the said exchanger in the opposite direction they become partially liquefied with backward return in the nest of tubes F; which is itself

also immersed in the vaporiser G. The slight gaseous residue from this liquefaction is extracted through the cock H, and consists for the greater part or substantially all of the nitrogen that was contained in the gases leaving the auxiliary column at W, while, the liquid produced, therefore, practically only contains oxygen and argon.

It is this liquid that is discharged at the top of the auxiliary column, but it will be observed that since, except for small losses, the liquid formed in the nest of tubes F is equivalent to the gas vaporised externally by the said nest of tubes, which rises in the column, there is no limit to the supply of liquid that may be made to flow through T'; it is an auxiliary closed circuit traversed indefinitely by the same quantity of gas which is constituted in this way. The flow of this circuit may, therefore, be incomparably greater than the flow of the liquid to be treated discharged through T, so that the phenomena of rectification in the auxiliary column will be essentially governed by this liquid, but very little by the one discharged at T. Now, this liquid formed at F is, as above remarked, constituted by a mixture of argon and oxygen more or less free from nitrogen. It follows from this that by the well known working of the phenomena of autopurification produced by the washing of the gases by means of a liquid resulting from the reliquefaction thereof, the gases escaping at W become when starting the operation richer and richer in the more volatile element of the system, viz: in argon.

As for the nitrogen contained in the mixture discharged through T, although on account of its greater volatility the whole of it reaches the top of the auxiliary column at W, its proportion remains very small on account of the comparatively greater flow of argon plus oxygen of the auxiliary circuit, and in consequence of its continual elimination as a gaseous residue in the nest of tubes F through N. It follows, therefore, that the gases extracted through W, if they do in truth always contain nitrogen, need only contain an exceedingly small proportion thereof, down to less than 1 per cent, if necessary, and they, therefore, constitute a mixture very rich in argon and practically free from nitrogen. The method may, however, be operated to retain a greater proportion of nitrogen in the circulating gas. When the normal operation is attained there may be withdrawn through Y a part of this mixture of argon and oxygen with or without a proportion of introgen corresponding practically to the whole of the argon introduced through T, and this constitutes one of the products of manufacture.

Thus it will be seen, that the liquid mixture of oxygen, argon and nitrogen to be treated is separated by this process into one fraction containing the greater part or substantially all the nitrogen escaping through H, another consisting of practically pure oxygen collected through U, and finally a third consisting of a mixture of argon and oxygen, more or less free from nitrogen, collected through Y.

It will be understood that if the vaporisation of the gases circulating in the rectifying column is accurately effected quantitatively by the liquefaction in the liquid oxygen of the recompressed gas—with the exception of the quantities of nitrogen and argon extracted—the vaporisation of the oxygen which constitutes one of the products of the manufacture, and which escapes through U, should be effected by means of coil S at the expense of the part of the air treated which is liquefied inside S. Of the treated air, therefore, about four-fifths ought to be liquefied in the system of tubes K, K' of the main apparatus, and about one-fifth in the system of tubes S of the compartment G whence the liquid produced is run up through T'' into the main column in order to compensate for loss of liquid oxygen through the tube T. Various changes and modifications in the details of application, as well as in the particular gaseous mixtures treated may be made within the scope of the present invention and of the annexed claims.

I claim:

1. A method of separating the constituents of a ternary gaseous mixture liquefying at low temperatures which comprises, subjecting a liquid and its vapors produced from said mixture and containing chiefly the least volatile constituent with a proportion of other volatile constituents to rectification by means of a liquid containing another and more volatile constituent, withdrawing the gaseous product of the rectification, separating a portion of the most volatile constituent from said gaseous product, liquefying the remaining gas, and using the liquid in said rectification.

2. A method of separating the constituents of a gaseous mixture liquefying at low temperatures which comprises, subjecting a liquid and vapors containing said constituents to rectification, compressing the gaseous effluent of this rectification, cooling it to separate one of the constituents from a liquid which is thereby impoverished in that constituent, and utilizing the impoverished liquid as a rectifying agent in said rectification.

3. A method of separating the constituents of a gaseous mixture liquefying at low temperatures which comprises, subjecting a liquid and vapors containing said constituents to continuing rectification, compressing the gaseous effluent, cooling it to separate a liquid containing chiefly two of said con-

stituents and a residue containing chiefly a third constituent, using the separated liquid, in said rectification, and withdrawing portions of said gaseous effluent when it is sufficiently enriched.

4. A method of recovering argon from air which comprises, subjecting a liquid and vapors containing oxygen, nitrogen and argon to continuing rectification, compressing the gaseous effluent, cooling it to separate a liquid containing chiefly argon and oxygen and a residue containing practically all of the nitrogen, using the last named liquid in said rectification, and repeating the operation.

5. A method of separating the constituents of a gaseous mixture liquefying at low temperatures which comprises, subjecting a liquid and vapors containing said constituents to rectification, thereby producing a liquid product rich in the least volatile constituent and a gaseous fraction, compressing this gaseous fraction, subjecting it in indirect contact with the liquid product to evaporate the latter and to simultaneously separate the liquefaction from the gaseous fraction a residue containing the most volatile constituent and a liquid containing chiefly two of said constituents, returning this liquid for further rectification, and repeating the operation.

6. A method of recovering argon from air which comprises, subjecting a liquid and vapors containing oxygen, nitrogen and argon to rectification, thereby producing a liquid product rich in oxygen and a gaseous fraction, compressing this gaseous fraction, subjecting it in indirect contact with the liquid oxygen to evaporate the latter and to simultaneously separate by liquefaction from the gaseous fraction a residue containing principally nitrogen and a liquid containing chiefly argon and oxygen, returning this liquid for further rectification, and repeating the operation.

7. A method of recovering argon from air which comprises, subjecting the vapors released from a liquid containing oxygen, nitrogen and argon and the said liquid to rectification by means of a liquid containing chiefly argon and oxygen, thereby producing a liquid product rich in oxygen and a gaseous fraction, withdrawing portions of the gaseous fraction when it is sufficiently enriched in argon, compressing the remainder of the gaseous fraction, subjecting it in indirect contact with the liquid rich in oxygen to evaporate the latter and to simultaneously separate by liquefaction from the gaseous fraction a residue containing principally nitrogen and a liquid containing chiefly argon and oxygen, and returning this liquid for further rectification.

8. A method of recovering argon from air, which comprises rectifying a liquid enriched in oxygen and containing nitrogen and argon, and subjecting the effluent from the rectification to selective liquefaction to separate nitrogen therefrom, rejecting the nitrogen and returning the liquid formed for further rectification.

9. A method of recovering argon from air, which comprises subjecting a liquid enriched in oxygen and containing nitrogen and argon to rectification, and thereafter causing the effluent from the rectification to travel in a closed circuit wherein it is successively subjected to selective liquefaction and to further rectification.

10. A method of recovering argon from air, which comprises causing the vapors evolving from a liquid rich in oxygen to be rectified by a liquid rich in argon and containing oxygen and nitrogen, so as to produce a liquid rich in oxygen and a gaseous mixture rich in argon and containing oxygen and nitrogen, and causing the gaseous mixture to travel in a closed circuit in which it is successively subjected to selective liquefaction and further rectification.

11. A method of recovering argon from air, which comprises causing the vapors evolving from a liquid rich in oxygen to be rectified by a liquid rich in argon so as to produce a liquid richer in oxygen and a gaseous mixture rich in argon, causing the gaseous mixture to travel in a closed circuit wherein it is successively subjected to selective liquefaction and further rectification, and withdrawing portions of the gaseous mixture when sufficiently enriched in argon.

12. A method of recovering argon from air, which comprises causing the vapors evolving from a liquid rich in oxygen to be rectified by a liquid rich in argon, whereby a liquid richer in oxygen and a gaseous mixture rich in argon are produced, withdrawing portions of the argon-enriched mixture, and causing the remainder of the mixture to travel in a closed circuit wherein it is successively subjected to selective liquefaction whereby nitrogen is separated and removed, and to further rectification.

13. A method of recovering argon from air, which comprises causing the vapors evolving from a liquid rich in oxygen to be rectified by a liquid rich in argon, thereby producing a liquid richer in oxygen and a gaseous mixture containing argon, nitrogen and oxygen, subjecting the gaseous mixture repeatedly to compression and to selective liquefaction with separation of the nitrogen, and utilizing the liquid produced by selective liquefaction as a rectifying agent for the incoming oxygen-enriched liquid.

14. A method of recovering argon from air, which comprises causing vapors from a liquid rich in oxygen to be rectified by a liquid rich in argon and containing oxygen and nitrogen so as to produce a liquid richer

in oxygen, which is further rectified into substantially pure oxygen and a gaseous mixture rich in argon, but containing some oxygen and nitrogen, warming the cold gaseous mixture by indirect contact with preceding portions of the same mixture after compression thereof, withdrawing portions of the gaseous mixture, compressing the remainder thereof, cooling the compressed gaseous mixture by indirect contact with succeeding portions thereof, liquefying the compressed gaseous mixture by indirect contact with a cooling medium, thereby separating substantially all of the nitrogen therefrom, using the resulting liquid to rectify the vapors of the oxygen-enriched liquid, and repeating the operation by causing the gaseous mixture rich in argon to travel in a closed circuit.

15. A method of recovering argon from air, which comprises subjecting a liquid rich in oxygen and containing nitrogen and argon supplied by the usual apparatus for separating air into oxygen and nitrogen, to vaporization and rectification, and in producing, by partial liquefaction with backward return of the effluent from the rectification, a gaseous fraction containing nitrogen, withdrawing the gaseous fraction, and utilizing the liquid resulting from the partial liquefaction as a rectifying agent for the liquid rich in oxygen, whereby the effluent from the rectification is enriched in argon.

16. A method of separating the constituents of gaseous mixtures liquefying at low temperatures which comprises, subjecting a liquid containing said constituents to continuing rectification, recompressing and refrigerating the gaseous effluent, to separate a liquid and a residual gaseous product containing another constituent withdrawing the residual gaseous product and returning the last mentioned liquid for further rectification, said gaseous effluent being thereby progressively enriched with a third constituent.

17. A method of recovering argon from the atmosphere, which comprises subjecting a liquid containing oxygen, nitrogen and argon to a cyclic operation including rectification to separate a liquid enriched in oxygen, with recompression and selective liquefaction of the gaseous effluent from the rectification to separate residual gaseous nitrogen, the remainder of said gaseous effluent being returned for further rectification and thereby progressively enriched in argon.

18. A method of separating the constituents of gaseous mixtures liquefying at low temperatures which comprises, subjecting a liquid containing said constituents to rectification, thereby producing a liquid product containing one of the constituents and a gaseous fraction containing two other constituents, compressing and cooling the gaseous fraction to produce a residual gaseous product containing another constituent and a liquid fraction withdrawing the residual gaseous product, and returning the liquid fraction for further rectification.

19. A method of separating the constituents of gaseous mixtures liquefying at low temperatures which comprises, subjecting a liquid containing said constituents to rectification, thereby producing a liquid product containing one of the constituents and a gaseous fraction containing two other contituents, compressing the gaseous fraction, subjecting it in indirect contact with the liquid product to evaporate the latter and to simultaneously produce by liquefaction of the gaseous fraction a residual gaseous product containing another of the constituents and a liquid fraction, withdrawing the residual gaseous product and returning the liquid fraction for further rectification.

20. A method of recovering argon from the atmosphere which comprises, subjecting a liquid containing oxygen, nitrogen and argon to rectification, thereby producing a liquid product containing principally oxygen and a gaseous fraction including argon and nitrogen, compressing the gaseous fraction, subjecting it to indirect contact with the liquid oxygen to evaporate the latter and to simultaneously produce by liquefaction of the gaseous fraction a residual gaseous product containing principally nitrogen and a liquid fraction including argon, withdrawing the residual gaseous product and returning the liquid fraction for further rectification.

In testimony whereof I have signed this specification in the presence of two subscribing witnesses.

GEORGES CLAUDE.

Witnesses:
EMILE LEDRET,
CHAS. P. PRESSLY.