G. CLAUDE.

PROCESS FOR SEPARATION OF THE CONSTITUENTS OF GASEOUS MIXTURES.

APPLICATION FILED FEB. 10, 1911.

1,068,219.

Patented July 22, 1913

2 SHEETS—SHEET 1.

Fig. 2.

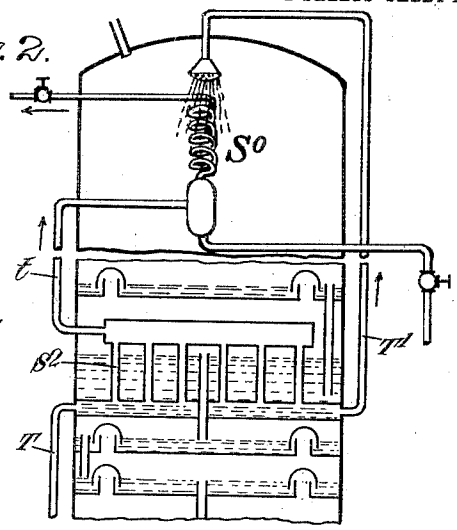


Fig. 1.

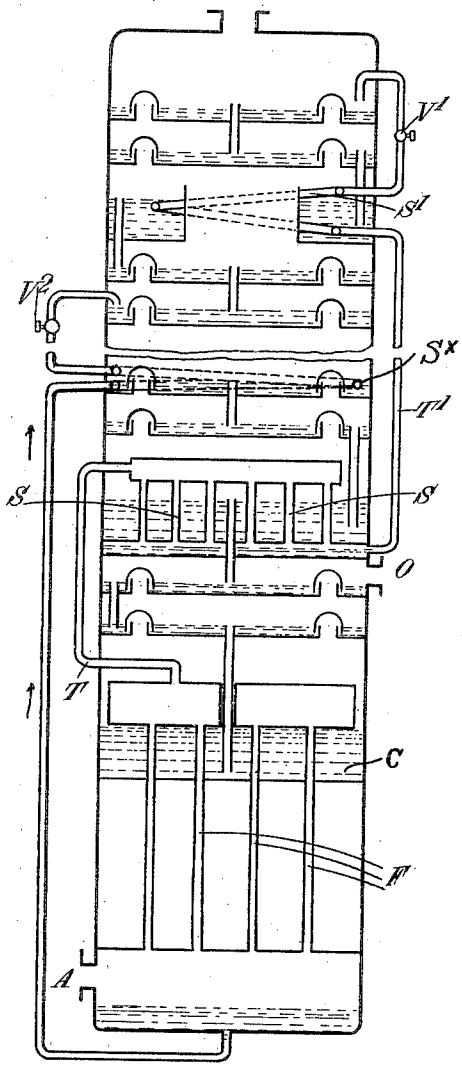
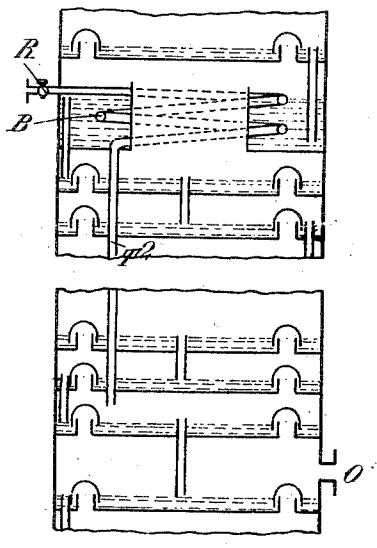


Fig. 3.



Witnesses.

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Inventor.

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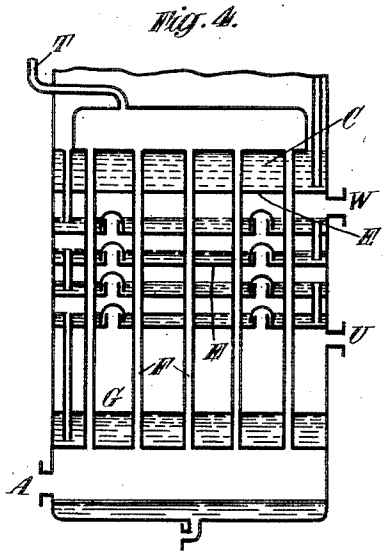
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2 SHEETS—SHEET 2.

Fig. 4.



Witnesses.

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UNITED STATES PATENT OFFICE.

GEORGES CLAUDE, OF PARIS, FRANCE, ASSIGNOR TO SOCIÉTÉ L'AIR LIQUIDE (SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE), OF PARIS, FRANCE.

PROCESS FOR SEPARATION OF THE CONSTITUENTS OF GASEOUS MIXTURES.

1,068,219. Specification of Letters Patent. Patented July 22, 1913.

Application filed February 10, 1911. Serial No. 607,775.

To all whom it may concern:

Be it known that I, GEORGES CLAUDE, a citizen of the Republic of France, residing at 48 Rue St. Lazare, Paris, in the Republic of France, have invented certain new and useful Improvements Relating to the Separation of the Constituents of Gaseous Mixtures, of which the following is a specification.

This invention relates to the separation of the constituents of gaseous mixtures, particularly of atmospheric air.

In my co-pending application, Serial No. 550,005, filed March 17, 1910, a process has been described in which the air from a single air supply passes in succession through two tubular systems at the foot of a rectification column. Two separate liquids, one rich in oxygen and the other rich in nitrogen, were thus produced and it was also pointed out that although the liquid rich in nitrogen contained a sufficiently high percentage of nitrogen to be satisfactory for most purposes, a liquid of still greater purity could be obtained by subjecting the gaseous residue escaping from the liquid rich in nitrogen to the cooling action of a liquid that was colder than either of the liquids used to produce the aforesaid two liquids rich in oxygen and in nitrogen respectively. For this purpose the cold liquid escaping directly from the bottom plate of the usual rectification column was used and liquid nitrogen of almost chemical purity was thereby obtained. The chief object of the present invention is to simplify this process and to increase the quantity of almost chemically pure nitrogen obtainable.

According to the present invention the gaseous mixture passes in succession through two tubular systems of which the first system is cooled by the liquid collected at the foot of the usual rectification column, but the liquefaction in the second tubular system is effected by using a liquid that has collected in the rectification column in a region situated some distance above the lowermost plate of the column and that is in course of rectification and is therefore colder than that collecting actually at the foot of the column. For this purpose the second tubular system is conveniently situated within the column at an intermediate point in its height, and may if desired be so arranged that liquefaction takes place in it on the principle of liquefaction with return flow of the liquid, as is the case in the first of the tubular systems. The two separate liquids before being introduced at appropriate points near the top of the column may be passed through cooling coils situated in the rectification column in a region above that where the respective liquefactions took place.

Further steps in the process relate to the treatment of the gaseous residues escaping from different parts of the column as hereinafter described.

In order that the invention may be clearly understood and readily carried into effect, the same will now be described more fully with reference to the accompanying drawings in which:—

Figure 1 illustrates diagrammatically one constructional form of apparatus adapted to operate in accordance with the invention. Fig. 2 is a view of a portion of the rectification column of the apparatus, in which a modified construction is adopted. Fig. 3 is a further view of a portion of the rectification column, showing also means for separating out argon, as hereinafter set forth. Fig. 4 is a modified form of the base of the rectification column.

Referring first to Fig. 1, it will be seen that the air, after being brought to the proper pressure and temperature, enters at A at the base of a vertical nest of tubes F, surrounded by liquid oxygen or liquid rich in oxygen which liquid has collected in a vaporizing vessel C at the base of the rectification column and undergoes evaporation therein; as pointed out in the prior specification, it is preferable that the upper part only of this nest of tubes F should be immersed in the liquid to be vaporized. The gaseous residue of the liquefaction with return flow of the liquid in this nest of tubes F ascends through a tube T and enters a second nest of tubes S immersed in some of the liquid of the rectification column at an intermediate point in the height of this column. The practically pure liquid nitrogen thus obtained in this second nest is conducted through a pipe T′ to the top of the rectification column, where it is discharged, and in order to prevent its partial evaporation at the moment of discharge, it is advis-

able to cool this liquid while still under pressure by circulating it in a cooling coil S′ arranged at a suitable point near the top of the rectification column. It may likewise be advantageous to cool under pressure, by means of a similar circulation in coil s^x the liquid rich in oxygen obtained in the first stage of the liquefaction of the air. The regulating cocks or valves V′ and V^2 through which these two liquids, namely the practically pure liquid nitrogen and the liquid rich in oxygen, flow on their way into the rectifying column, are arranged beyond their respective cooling coils. If it is found that the total area of the condensation surface of the tubes S is at any time excessive, this area may be reduced by regulating the valve V′ in such a manner as to cause some liquid to collect in the lower part of the tubes S, thus reducing their effective area for condensation.

The practical execution of this process is subjected to the following observation: When it is desired to obtain nitrogen in a practically pure state, the rectification work of the column and the steadiness of the operation are greatly facilitated if, instead of withdrawing the oxygen as gas in a practically pure state, it is withdrawn with a certain quantity of nitrogen, that is to say in the state of eighty per cent. oxygen for example. However, the advantage thus secured would entail a defect in that the liquid, which, under these conditions, falls from the last plate of the rectification column into the vaporizing vessel C, instead of being almost pure oxygen, would necessarily be only at a percentage corresponding to that of the extracted gas, that is to say, eighty per cent. oxygen for example. In practice, on account of the unavoidable disturbances incidental to working (such as variations in the supply of compressed air, etc.,) the percentage of this liquid undergoes appreciable fluctuations, for example from seventy to ninety per cent., and its boiling point naturally undergoes also corresponding variations. As this temperature (the boiling point) is just the one at which the liquefaction of the incoming air requires to be carried out in the tubes of the vaporizing vessel C, this actual liquefaction would thus be constantly disturbed; this would result in a continuous irregularity in the working of the apparatus and a difficult management which might counterbalance the advantage referred to above as being derived by withdrawing gas containing eighty per cent. of oxygen. In order to obviate this defect, an advantageous procedure is as follows: Instead of withdrawing the gaseous oxygen at the level of the vaporizing vessel C, impure oxygen is withdrawn at a higher level, for example at the level of the second or third plate from the base of the rectification column, as indicated at O. Under such conditions the liquid of the column will reach the level of the oxygen outlet with a composition which is necessarily equal to that of the oxygen withdrawn—say eighty per cent. oxygen by way of example—but this liquid is rapidly converted into liquid oxygen as it completes its descent of the column owing to its meeting with the whole of the gaseous oxygen which ascends in this part of the column; hence, in this manner, the vaporizing vessel is supplied with liquid oxygen of the desired purity, the temperature of which is almost invariable.

In the foregoing description it has been assumed that the gases to be liquefied are conducted in an upward direction by the first nest of tubes and in a downward direction by the second nest of tubes. If, however, it is desired to obtain gases of extremely low boiling point, such as neon, or helium, it is preferable for the second nest of tubes to conduct the gases in an upward direction so that the liquefaction in these tubes can take place with return flow of the liquid. Such an arrangement is illustrated in Fig. 2, in which the second part of the tubular system consists of an ascending nest of tubes S^2 into which the gas to be liquefied is introduced at the bottom and after becoming liquid flows backward. The gaseous residue, rich in neon and helium, which reaches the summit of these tubes, can then be collected at the exterior, or sent under pressure through a tube *t* toward a device S°, in which the said residue undergoes a last enrichment.

It may be desirable to effect a withdrawal of a high proportion of the argon contained in the air treated, which argon would otherwise mingle partly with the oxygen and partly with the nitrogen. Now the volatility of argon is intermediate between that of oxygen and that of nitrogen. The argon is forced toward the base of the rectification column by the stream of liquid nitrogen discharged into the column at the summit of the latter and tends to accumulate, in part, with the oxygen in the vaporizing vessel and to such an extent that the principal impurity of the oxygen near the base of the column is constituted by argon and not by nitrogen. Nevertheless this argon, being more volatile than the oxygen, does not concentrate without difficulty in the actual liquid oxygen, but accumulates rather on the lower plates of the column, to an extent which may reach ten per cent. In short, during the first few hours of the operation of the apparatus, an actual accumulation of argon takes place on these last plates, and it is when this accumulation suffices to produce a sufficiently high vapor pressure of the argon, that this gas is able to escape, partly to the oxygen,

and partly to the nitrogen, and to such an extent as to counterbalance the fresh quantities of argon which occur in the air to be treated and which are therefore being constantly supplied in proportion to the constant supply of air. The method adopted for remedying this condition of affairs consists broadly in providing a special door of escape for the argon; one method of doing so is illustrated diagrammatically in Fig. 3 and consists in conducting, by a tube T^2, some of the gases rich in argon, existing above one of the lower plates of the rectification column, through a coil B immersed in the relatively cold liquid which is situated at about the upper third of this column. The oxygen of these gases liquefies with return flow of the liquid in the coil B and flows back automatically toward the plate from which the gas comes, while the gaseous residue, which is very rich in argon, is withdrawn in the desired proportion, by suitably opening the cock R, and is collected outside after having yielded up its cold if necessary. The coil should not be arranged in the exceedingly cold zones of the column because the argon might solidify there, as its point of congelation is—190° C. approximately. It is obvious that this method of purifying the gases of the rectification column is applicable, whatever may be the method adopted for liquefying the compressed air supplied at the foot of the column.

In the above description it has been assumed that liquid rich in oxygen collects at the foot of the rectification column in a vaporizing vessel, and that this vessel surrounds the upper part of the first nest of tubes. If it were desired to obtain some practically pure oxygen, a short additional rectification column as illustrated by the plates E in Fig. 4 might be arranged beneath the main vaporizing vessel C and around the aforesaid nest of tubes F, and the liquid rich in oxygen might be made to overflow the main vaporizing vessel and descend the short additional rectification column beneath it. The practically pure oxygen thereby produced and collected in the compartment G surrounding the lower end of the tubes F at the foot of this short additional rectification column is allowed to undergo a final vaporization; part of the resulting vapor is withdrawn, as practically pure oxygen, through the opening U, and used for any desired purpose, and the remainder, containing a certain proportion of nitrogen, can be drawn out of the column through the opening W, after having assisted in the above mentioned additional rectification.

What I claim is:—

1. A process for the separation of a mixture of gases, such as air, into its constituents by way of liquefaction followed by rectification of the liquid produced, consisting in passing the compressed and cooled gases through a laterally confined space cooled by liquid collected at the foot of the usual rectification column, and then passing the remaining unliquefied gases in continuation through a second laterally confined space cooled by liquid collected in the column in a region situated some distance above the foot of the column.

2. A process for the separation of a mixture of gases, such as air, into its constituents by way of liquefaction followed by rectification of the liquid produced, consisting in passing the compressed and cooled gases through an upwardly conducting laterally confined space cooled by liquid collected at the foot of the rectification column, and then passing the remaining unliquefied gases in continuation through a second upwardly conducting laterally confined space cooled by liquid collected in the column in a region situated some distance above the foot of the column.

3. A process for the separation of a mixture of gases, such as air, into its constituents by way of liquefaction followed by rectification of the liquid produced, consisting in temporarily arresting and collecting the liquid at an intermediate point in its descent of the usual rectification column, passing the compressed and cooled gases through an upwardly conducting laterally confined space cooled by liquid collected at the foot of the column, and then passing the remaining unliquefied gases in continuation through a second laterally confined space cooled by the aforesaid temporarily arrested and collected liquid.

4. A process for the separation of a mixture of gases, such as air, into its constituents by way of liquefaction followed by rectification of the liquid produced, consisting in passing the compressed and cooled gases through an upwardly conducting laterally confined space the upper part of which is kept at a lower temperature than the lower part by surrounding the upper part with liquid collected at the foot of the usual rectification column, and then passing the remaining unliquefied gases in continuation through a second laterally confined space cooled by liquid collected in the column in a region situated some distance above the foot of the column.

5. A process for the separation of a mixture of gases, such as air, into its constituents by way of liquefaction followed by rectification of the liquid produced, consisting in passing the compressed and cooled gases through an upwardly conducting laterally confined space the upper part of which is kept at a lower temperature than the lower part by surrounding the upper

part with liquid collected at the foot of the usual rectification column, and then passing the remaining unliquefied gases in continuation through a second upwardly conducting laterally confined space cooled by liquid collected in the column in a region situated some distance above the foot of the column.

6. A process for the separation of a mixture of gases, such as air, into its constituents by way of liquefaction followed by rectification of the liquid produced, consisting in passing the compressed and cooled gases through an upwardly conducting laterally confined space cooled by liquid collected at the foot of the rectification column, then passing the remaining unliquefied gases in continuation through a second laterally confined space cooled by liquid collected in the column in a region situated some distance above the foot of the column, passing the two liquids produced in the aforesaid confined spaces into the rectification column at its upper part and conducting one of the two liquids through a laterally confined space on its way to the rectification column, said space being situated in the column at a point above that where the production of the liquid took place.

7. A process for the separation of a mixture of gases, such as air, into its constituents by way of liquefaction followed by rectification of the liquid produced, consisting in passing the compressed and cooled gases through an upwardly conducting laterally confined space cooled by liquid collected at the foot of the rectification column, then passing the remaining unliquefied gases in contiuation through a second laterally confined space cooled by liquid collected in the column in a region situated some distance above the foot of the column, passing the two liquids produced in the aforesaid confined spaces into the rectification column at its upper part, and conducting each of the two liquids through a laterally confined space on its way to the rectification column, said space being situated in the column at a point above that where the production of the liquid took place.

8. A process for the separation of a mixture of gases, such as air, into its constituents by way of liquefaction followed by rectification of the liquid produced, consisting in passing the compressed and cooled gases through an upwardly conducting laterally confined space cooled by liquid collected at the foot of the rectification column, then passing the remaining unliquefied gases in continuation through a second upwardly conducting laterally confined space cooled by liquid collected in the column in a region situated some distance above the foot of the column, and passing the remaining unliquefied gases through a third upwardly conducting laterally confined space cooled to a lower temperature than that of the first and second confined spaces, for obtaining rare gases.

9. A process for the separation of a mixture of gases, such as air, into its constituents by way of liquefaction followed by rectification of the liquid produced, consisting in passing the compressed and cooled gases through an upwardly conducting laterally confined space cooled by liquid collected at the foot of the rectification column, then passing the remaining unliquefied gases in continuation through a second laterally confined space cooled by liquid collected in the column in a region situated some distance above the foot of the column, passing some of the gases liberated near but slightly above the foot of the column through an upwardly conducting laterally confined space cooled by the liquid descending the column at its upper part, returning to the column the liquid produced in the last mentioned confined space, and conducting the unliquefied gaseous residue, rich in argon, out of the said space and away from the column.

10. A process for the separation of a mixture of gases, such as air, into its constituents by way of liquefaction followed by rectification of the liquid produced, consisting in passing the compressed and cooled gases through an upwardly conducting laterally confined space cooled by liquid collected at the foot of the rectification column, then passing the remaining unliquefied gases in continuation through a second laterally confined space cooled by liquid collected in the column in a region situated some distance above the foot of the column, passing the two liquids produced in the aforesaid confined spaces into the rectification column at its upper part, and subjecting the liquid collected at the foot of the rectification column to an additional rectification in the neighborhood of the first of the above mentioned laterally confined spaces through which the compressed and cooled gases are conducted.

11. A process for the separation of a mixture of gases, such as air, into its constituents by way of liquefaction followed by rectification of the liquid produced, consisting in passing the compressed and cooled gases through an upwardly conducting laterally confined space cooled by liquid collected at the foot of the rectification column, passing the two liquids produced in the aforesaid confined spaces into the rectification column at its upper part, subjecting the liquid collected at the foot of the rectification column to an additional rectification in the neighborhood of the first of the above mentioned laterally confined spaces through which the compressed and cooled gases are

conducted, collecting the liquid resulting from this additional rectification, withdrawing part of the vapor arising from it direct away from the rectification column, and conducting the remaining vapor upward in contact with the descending liquid undergoing the said additional rectification.

12. A process for the separation of a mixture of gases, such as air, into its constituents by way of liquefaction followed by rectification of the liquid produced, consisting in passing the compressed and cooled gases through an upwardly conducting laterally confined space cooled by liquid collected at the foot of the rectification column, then passing the remaining unliquefied gases in continuation through a second laterally confined space cooled by liquid collected in the column in a region situated some distance above the foot of the column, and withdrawing, at a point in the column a short distance above the foot of the same, some of the vapor of the liquid undergoing rectification as it reaches that point.

In testimony whereof I affix my signature is presence of two witnesses.

GEORGES CLAUDE.

Witnesses:

PIERRE HOURLIER,

DEAN B. MASON.