April 2, 1940. E. GOMONET 2,195,987

RECOVERY OF KRYPTON AND XENON FROM THE ATMOSPHERE

Filed March 27, 1937

Fig. 1.

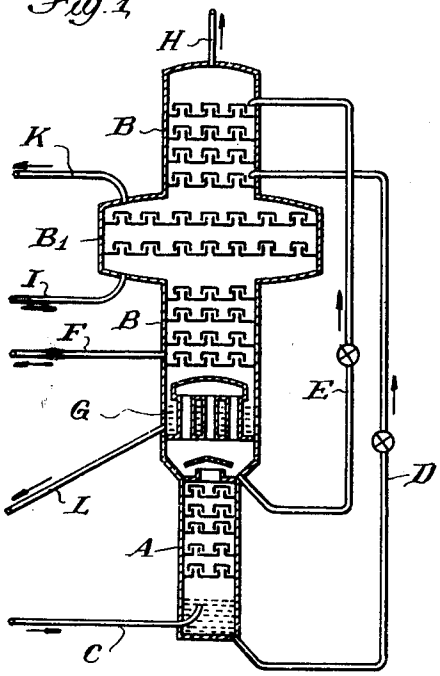


Fig. 2.

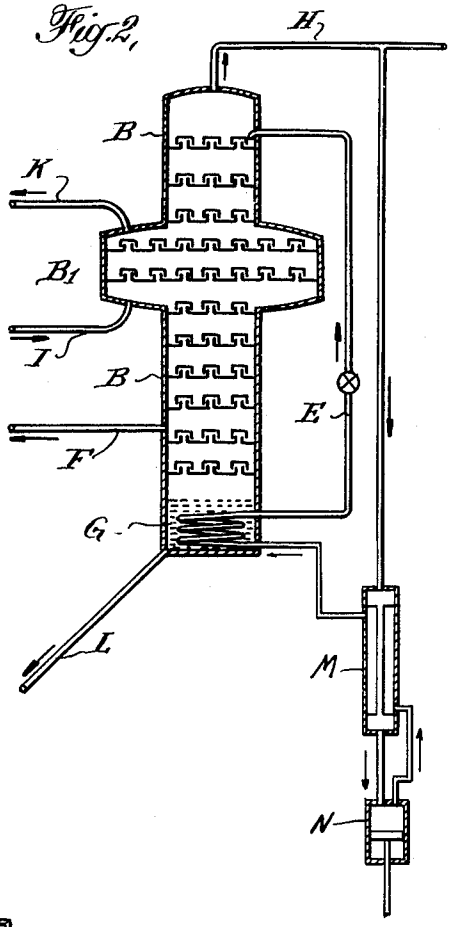
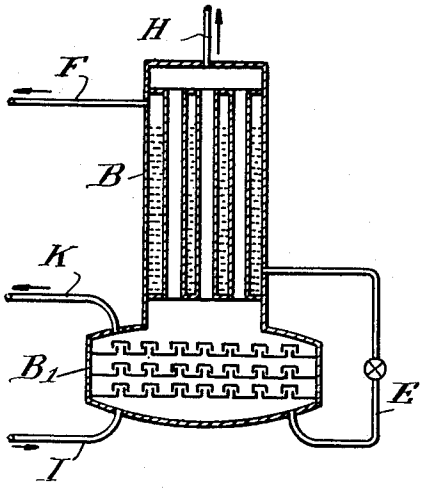


Fig. 3.



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RECOVERY OF KRYPTON AND XENON FROM THE ATMOSPHERE

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9 Claims. (Cl. 62—175.5)

This invention relates to the separation and recovery of krypton and xenon from the atmosphere and particularly to improvements in the process whereby recovery is facilitated.

It is known that the krypton contained in air may be extracted therefrom by washing the air with a relatively small quantity of a liquid mixture of oxygen and nitrogen, for instance a quantity of washing liquid smaller than $\frac{1}{10}$ of the quantity of the washed air. The liquid utilized for the washing takes up, in the course of the same, all or nearly all the krypton contained in the washed gaseous air. This liquid is then wholly or nearly wholly vaporized, and the krypton carried along by the vaporized gas is retained by subjecting the same to a rectification. A small quantity of liquid or gas containing nearly the whole of the krypton contained in the gaseous air subjected to the washing operation is finally collected. It is also known that a small portion of the oxygen contained in the washed gaseous air may be simultaneously extracted therefrom.

This invention relates to a process in which there is obtained, at the same time as the krypton, a certain amount of nitrogen. The novel process consists in a combination of the hereinbefore mentioned process for extracting krypton and of the known general process for extracting from the air the whole or a part of its nitrogen in the gaseous state by liquefaction and rectification. In this known general process, whichever particular method is adopted, gaseous nitrogen in a substantially pure state can be obtained only by providing for the formation of washing liquid nitrogen in a substantially pure state which is utilized for washing a gas consisting of the air itself to be separated into its constituents or a gaseous mixture of oxygen and nitrogen obtained from this air by preliminary operations. The air or the gaseous mixture of oxygen and nitrogen are thereby transformed into substantially pure gaseous nitrogen, whereas the liquid nitrogen is transformed into a liquid mixture of oxygen and nitrogen.

This invention rests on the property which this liquid mixture possesses of being capable of washing out krypton from a quantity of air substantially larger than that of the washing liquid itself. According to the present invention, in the known extraction from the air of all or part of its nitrogen in the gaseous state by liquefaction and rectification by means of liquid nitrogen, there is washed, by the liquid mixture of oxygen and nitrogen into which this liquid nitrogen is transformed in the course of the rectification, a quantity of air which is large in proportion to that of this liquid mixture, so as to extract therefrom its krypton in known way; this large quantity will in practice amount to at least five times, and preferably be of the order of twenty times, the quantity of the liquid mixture of oxygen and nitrogen utilized for the washing.

Three ways of carrying out this invention are shown in the accompanying drawing, in which:

Fig. 1 indicates diagrammatically the process in which air is separated into oxygen and nitrogen by a two-stage rectification;

Fig. 2 is a similar illustration of a process in which one rectification is employed; and

Fig. 3 is a diagrammatic illustration of another procedure.

In Fig. 1, A represents the pressure column utilized for the preliminary separation of air into liquid nitrogen and a liquid containing about 40% of oxygen, and B the column under the atmospheric pressure in which the final separation into oxygen and nitrogen takes place. The air to be separated into its components is introduced at C at the bottom of the column A. It ascends therein and becomes progressively richer and richer in nitrogen, so that it reaches the top of this column as substantially pure nitrogen. This nitrogen is liquefied by heat exchange with the krypton-enriched liquid oxygen obtained by the final separation of the air carried out under lower pressure in the rectification column B. A portion of this liquefied nitrogen flows backwards through the rectification column A and reaches its bottom as a liquid mixture of oxygen and nitrogen containing approximately 40% of oxygen. The 40%-oxygen-containing liquid is conveyed to an intermediate place of the column B through the pipes D and the remaining portion of the liquefied nitrogen to the top of the column B through the pipe E, the pressure of the two liquid fractions being simultaneously relieved. These two fractions are rectified in the column B so that they reach the bottom of this column as krypton-enriched liquid oxygen, which, as mentioned above, is vaporized by heat exchange with the gaseous nitrogen under pressure in the column A. A portion of the vaporized oxygen is extracted at F in the gaseous state in the vicinity of the vaporizer G at the bottom of the column B, whereas the remaining portion rectifies the mixture of both aforementioned liquids delivered to the column B, whereby it is transformed into a gaseous mixture of oxygen and nitrogen.

The column B comprises a part B_1 of enlarged section through which a quantity of air important

in proportion to that of the air introduced at C, say twenty times the latter quantity, is passed. The latter large quantity of air enters the enlarged part B_1 at I, combines there with the gaseous mixture of oxygen and nitrogen rising from the bottom of the column and leaves the enlarged part B_1 at K after having given up its krypton to the liquid which flows downwards through the part B_1 of the column B and reaches the vaporizer G. This krypton, in admixture with that of the air introduced at C, is extracted in known way. For instance, a small quantity of liquid krypton-rich oxygen is extracted at L from the vaporizer G. The gaseous oxygen collected at F may also be allowed to carry along all the krypton, and this is extracted in known way from the gaseous oxygen by adsorption or rectification. As to that portion of the gas ascending through the enlarged portion B_1 which is not withdrawn at K, it is allowed to rise further through the upper part of the column B in countercurrent to the liquid nitrogen delivered through the pipe E and is thus converted into substantially pure nitrogen, which is collected at the top of the column.

In the process for separating air by a two-stage rectification which is here used, the bulk of the two liquids delivered through the two pipes D and E to the low-pressure column B is, as known, capable of separating into its constituents a certain amount of air directly introduced into this column. The quantity of air leaving at K can therefore be smaller than the quantity of air entering at I. It should be noted that the passage through the column B_1 of a very large quantity of air entering at I and leaving wholly or partly at K prevents the accumulation of argon in this column, inasmuch as it is considerably larger than that which is sufficient for obtaining the same result in the process of the applicant's pending U. S. application Ser. No. 709,674, filed February 3, 1934. That portion of the air entering at I which is not extracted at K and flows upwards in the upper part of the column B can thus amount to the quantity of the supplementary air which can be introduced into the column and separated therein into its components according to this specification.

In the example in accordance with Fig. 1, the air from which the krypton is to be extracted is washed by the bulk of the two liquids delivered to the column B. But it might also be washed outside this column only by the liquid mixture of oxygen and nitrogen which is collected at the bottom of the pressure column A, this liquid being introduced into the column B after it has been utilized for the washing of the gaseous air.

In the process according to Fig. 2, one rectification column only is utilized. The air to be treated is introduced at I; the largest portion, say nine-tenths, of this air, leaves at K after having flown through the enlarged portion B_1 of the column, and thereby given up its krypton to the downflowing liquid and the remaining part flows further upwards through the upper part of the column and leaves at H as substantially pure nitrogen. A part of this nitrogen is warmed up to the surrounding temperature in the heat-exchanger M, compressed in a compressor N including the usual means for removing the heat of compression, cooled down back to a low temperature in the heat-exchanger M by heat exchange with the nitrogen to be compressed, liquefied in the vaporizer G at the bottom of the column B, and delivered through the pipe E to the top of the column B, the pressure of the nitrogen thus liquefied being simultaneously relieved. The krypton-enriched liquid mixture of oxygen and nitrogen with which the air has been washed is allowed to further downflow through the lower portion of the rectification column B. It reaches the bottom of this column as substantially pure krypton-enriched liquid oxygen which, as stated above, is nearly wholly vaporized by heat exchange with a portion of the gaseous nitrogen withdrawn at H. A portion of this vaporized oxygen is withdrawn at F and the remaining portion ascends through the lower part of the rectification column B, being thereby transformed into a gaseous mixture of oxygen and nitrogen, which mixture combines with the air admitted at I. The small quantity of non-vaporized liquid oxygen is withdrawn at L. It contains the krypton to be recovered.

Fig. 3 shows the process of the invention in the case in which air is separated by the process known in the art as "backward return" into nitrogen and a mixture of oxygen and nitrogen containing about 50% of oxygen. The air is passed at I to the bottom of a washing column B_1. The largest part say nine-tenths, of this air, leaves at K at the top of the column B_1 after having given up its krypton to the liquid which flows downwards through the column. The rest of the air, say one-tenth, flows upwards through a nest of backward return tubes B which is cooled outwardly by the liquid which has been collected at the bottom of the column B and delivered upwards through the pipe E. Under the influence of the cooling, the air which flows through the nest of tubes is partly liquefied and the liquid formed falls backward, at the same time washing the ascending gas; when this liquid has reached the bottom of the nest of tubes B it constitutes the above mentioned liquid which flows downwards through the column B_1. The liquid condensing from the gas rising in the tubes B is richer in oxygen than the gas from which it condenses, and this results in the ascending gas becoming richer and richer in nitrogen as it flows upward, so that it finally consists of substantially pure nitrogen when it reaches the top of the tubes. The liquid condensing from the gas at the top of the tubes also consists of substantially pure nitrogen, which grows richer and richer in oxygen as it flows downward. Nitrogen is collected through a pipe H at the top of the nest of tubes B. The gas resulting from the vaporization, taking place around the tubes B, of the 50%-oxygen-liquid is collected at F. It is then subjected in known manner to a partial recondensation with rectification so as to obtain its krypton.

I claim:

1. The process of simultaneously recovering nitrogen and krypton from the atmosphere which comprises washing with liquid nitrogen gaseous air in a quantity substantially greater than that of the liquid nitrogen, whereby the air gives up its krypton to the washing liquid, removing from contact with the washing liquid a portion of the air at least as great as that of the washing liquid from whose contact this portion is removed, allowing the rest of the air to be further washed by the liquid, whereby said rest is transformed into substantially pure nitrogen, and vaporizing the krypton-enriched liquid with which the air has been washed.

2. The process of simultaneously recovering nitrogen and krypton from the atmosphere which comprises washing with liquid nitrogen gaseous

air in a quantity substantially greater than that of the liquid nitrogen, whereby the air gives up its kryton to the washing liquid, removing from contact with the washing liquid a portion of the air at least as great as that of the washing liquid from whose contact this portion is removed, allowing the rest of the air to be further washed by the liquid, whereby said rest is transformed into substantially pure nitrogen, recovering by heat exchange the cold of the obtained substantially pure gaseous nitrogen, compressing a portion of said nitrogen, cooling said portion by heat exchange with the cold gaseous products of the separation of the treated air into its constituents, liquefying said portion by heat exchange with the krypton-enriched liquid with which the gaseous air has been washed, which is thereby vaporized, relieving the pressure of the nitrogen thus liquefied and utilizing said liquid nitrogen as said washing liquid for the gaseous air.

3. The process of simultaneously recovering nitrogen and krypton from the atmosphere which comprises washing with liquid nitrogen gaseous air in a quantity substantially greater than that of the liquid nitrogen, whereby the air gives up its krypton to the washing liquid, removing from contact with the washing liquid a portion of the air at least as great as that of the washing liquid from whose contact this portion is removed, allowing the rest of the air to be further washed by the liquid, whereby said rest is transformed into substantially pure nitrogen, further rectifying the liquid with which the air has been washed so as to transform it into a krypton-enriched oxygen-rich liquid, recovering by heat exchange the cold of the obtained substantially pure gaseous nitrogen, compressing a portion of said nitrogen, cooling said portion by heat exchange with the cold gaseous products of the separation of the treated air into its constituents, liquefying said portion by heat exchange with the above mentioned krypton-enriched oxygen-rich liquid, relieving the pressure of the nitrogen thus liquefied and utilizing said liquid nitrogen as said washing liquid for the gaseous air.

4. The process of simultaneously recovering nitrogen and krypton from the atmosphere which comprises washing gaseous air with liquid nitrogen condenser from the ascending air by cooling, whereby the air gives up its krypton to the washing liquid, removing from contact with the washing liquid the greater portion of the air, allowing the rest of the air to further ascend while being subjected to an external cooling, whereby the liquid with which the air is washed condenses from said rest, relieving the pressure of the krypton-enriched liquid with which the air has been washed and utilizing this liquid as said external cooling means for the above mentioned rest of the air subjected to external cooling, whereby said krypton-enriched liquid is vaporized.

5. The process of simultaneously recovering nitrogen and krypton from the atmosphere which comprises washing a gaseous mixture of oxygen and nitrogen with liquid nitrogen, whereby the liquid nitrogen is transformed into a liquid mixture of oxygen and nitrogen and the gaseous mixture of oxygen and nitrogen is transformed into substantially pure gaseous nitrogen, collecting said nitrogen in the gaseous state, further washing with the liquid mixture of oxygen and nitrogen gaseous air in a quantity substantially greater than that of said liquid mixture, whereby the air gives up its krypton to the washing liquid, and vaporizing the krypton-enriched liquid with which the air has been washed.

6. The process of simultaneously recovering nitrogen and krypton from the atmosphere which comprises preliminarily separating air by liquefaction and rectification carried out under pressure into a first portion consisting of a liquid mixture of oxygen and nitrogen richer than air in oxygen and a second portion consisting of gaseous nitrogen, liquefying said second portion by heat exchange with the krypton-enriched liquid oxygen obtained by the final separation of the air carried out under low pressure, relieving the pressure of both liquid portions, rectifying said second liquid portion, whereby said second liquid portion is transformed into a liquid mixture of oxygen and nitrogen, washing with said transformed second liquid portion gaseous air in a quantity substantially greater than that of said second liquid portion, whereby the air gives up its krypton to the washing liquid, combining both liquid portions rectifying the krypton-enriched mixture of both liquid portions so as to transform it into the above mentioned krypton-enriched liquid oxygen, vaporizing said krypton-enriched liquid oxygen by said heat exchange with the above mentioned gaseous nitrogen under pressure, and utilizing said vaporized gas for the above mentioned rectification of first the krypton-enriched mixture of both liquid portions and then the second liquid portion alone whereby said vaporized gas is successively transformed first into a gaseous mixture of oxygen and nitrogen and then into substantially pure nitrogen.

7. The process of simultaneously recovering nitrogen and krypton from the atmosphere which comprises preliminarily separating air by liquefaction and rectification carried out under pressure into a first portion consisting of a liquid mixture of oxygen and nitrogen richer than air in oxygen and a second portion consisting of gaseous nitrogen, liquefying said second portion by heat exchange with the krypton-enriched liquid oxygen obtained by the final separation of the air carried out under lower pressure, relieving the pressure of both liquid portions, rectifying said second liquid portion, whereby said second liquid portion is transformed into a liquid mixture of oxygen and nitrogen, combining said transformed second liquid portion with the first liquid portion, washing with the mixture of both liquid portions gaseous air in a quantity greater than that of said mixture, whereby this gaseous air gives up its krypton to said washing liquid mixture, rectifying the krypton-enriched mixture of both liquid portions so as to transform it into the above mentioned krypton-enriched liquid oxygen, vaporizing said krypton-enriched liquid oxygen by said heat exchange with the above mentioned gaseous nitrogen under pressure, and utilizing said vaporized gas for the above mentioned rectification of first the krypton-enriched mixture of both liquid portions and then the second liquid portion alone whereby said vaporized gas is successively transformed first into a gaseous mixture of oxygen and nitrogen and then into substantially pure nitrogen.

8. The process of simultaneously recovering nitrogen and krypton from the atmosphere which comprises passing gaseous air upwardly while subjecting it to cooling whereby liquid nitrogen condenses from and washes the ascending air, collecting in the gaseous state the uncondensed gaseous nitrogen resulting from said washing, washing with the liquid with which the ascending air

has been washed a quantity of air substantially greater than that of the washing liquid, whereby said air gives up its kryton to the washing liquid, relieving the pressure of said krypton-enriched washing liquid and utilizing this krypton-enriched liquid as external cooling means for the air subjected to external cooling, whereby said krypton-enriched liquid is vaporized.

9. The process of simultaneously recovering nitrogen and krypton from the atmosphere which comprises preliminarily separating air by liquefaction and rectification carried out under pressure into a first portion consisting of a liquid mixture of oxygen and nitrogen richer than air in oxygen and a second portion consisting of gaseous nitrogen, liquefying said second portion by heat exchange with the liquid krypton-enriched oxygen obtained by the final separation of the air carried out under lower pressure, relieving the pressure of both liquid portions, rectifying said second liquid portion so as to transform it into a liquid mixture of oxygen and nitrogen, combining said transformed second liquid portion with said first liquid portion, washing with the liquid mixture thus constituted gaseous air in a quantity substantially greater than that of said liquid mixture whereby this gaseous air gives up its krypton to said liquid mixture, rectifying said krypton-enriched liquid mixture so as to transform it into the above mentioned krypton-enriched liquid oxygen, vaporizing said krypton-enriched liquid oxygen by said heat exchange with the above mentioned gaseous nitrogen under pressure, utilizing said vaporized gas for said rectification of said krypton-enriched liquid mixture whereby said vaporized gas is transformed into a gaseous mixture of oxygen and nitrogen, admixing said gaseous mixture with the afore mentioned gaseous air before subjecting said air to the above mentioned washing, removing from contact with the mixture of both liquid portions a portion of the gaseous mixture resulting from said admixture at least as great as that of the liquid from whose contact this portion is removed, and utilizing the rest of said gaseous mixture for the above mentioned rectification of the second liquid portion, whereby said rest is transformed into substantially pure nitrogen.

EUGENE GOMONET.

CERTIFICATE OF CORRECTION.

Patent No. 2,195,987. April 2, 1940.

EUGENE GOMONET.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 38, for the word "pipes" read --pipe--; page 3, first column, line 49, claim 4, for "condenser" read --condensed--; and second column, line 55, claim 7, strike out "krypton-enriched" and insert the same after "liquid" in line 54, same claim; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of May, A. D. 1940.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.