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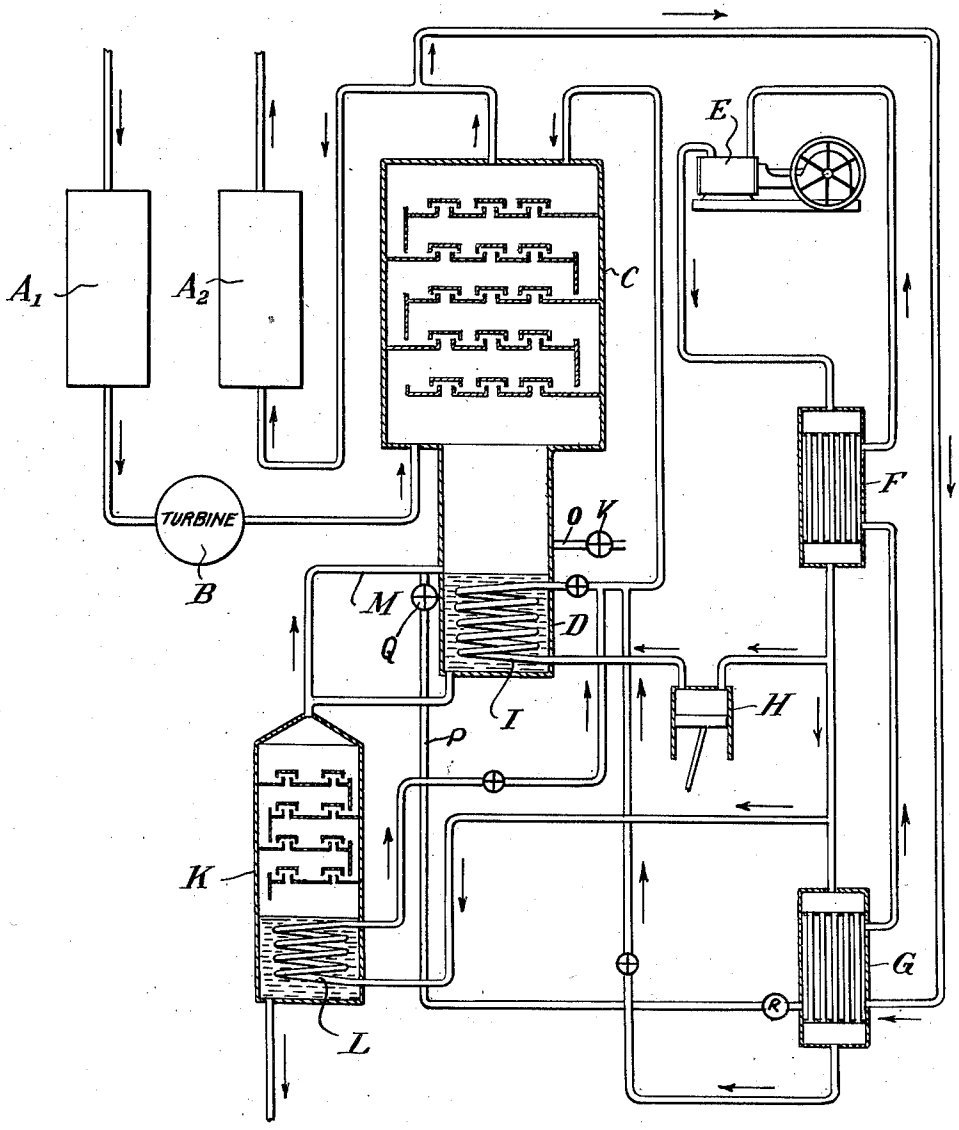

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PROCESS FOR OBTAINING KRYPTON AND XENON FROM AIR

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The krypton and the xenon which are contained in very minute proportions in atmospheric air are, as known, less volatile than all the other constituents of the air. They therefore collect in the oxygen when atmospheric air is treated by liquefaction and rectification in order to obtain its oxygen in a more or less pure state. Until now it is only from this krypton and xenon containing oxygen that both these gases have been extracted. But the quantities of krypton and xenon which can thus be obtained are very small and cannot meet all the applications to which the peculiar properties of these gases may give rise, for instance the filling of gas-containing glow lamps.

In the process of this invention, krypton and xenon are directly extracted from atmospheric air without the latter having been subjected to a previous separation. This process consists in directly subjecting atmospheric air, which has previously been cooled down to the neighbourhood of its dew point, to a rectification by a washing liquid consisting of a liquefied gas more volatile than krypton or by a mixture of such liquefied gases, the washing liquid being preferably utilized in a quantity large enough to allow the retention of substantially the whole of the krypton and the xenon, but nevertheless small in proportion to the treated air, and in concentrating in krypton and xenon the liquid resulting from the rectification by vaporizing nearly the whole of it.

The washing liquid is preferably air which has formerly been freed from its krypton (for the sake of simplicity xenon will no longer be mentioned henceforth) but it could also be nitrogen or oxygen or a mixture of these two substances in any proportions. The quantity of the washing liquid may be less than the tenth part of the quantity of the treated air. If the washing liquid contains no krypton the air may be completely free from krypton after its treatment.

The providing of the heat which is necessary for vaporizing the krypton-containing liquid preferably takes place in known manner by means of a substantially equivalent quantity of a cold gas which liquefies as the liquid vaporizes and is chosen of such a nature that the liquid resulting from its liquefaction may be used as a rectifying liquid for the treated air. This cold gas may consist of a part of the air which has been subjected to the rectification.

If desired, there may be obtained, at the same time as krypton, a gas rich in oxygen which, when the rectifying liquid does not contain a substantial proportion of constituents less volatile than oxygen, as is generally the case, may be substantially pure oxygen. To this effect one needs but to insert a few rectifying trays on the common way which is followed by the liquid and the gas between the washing column and the vaporizer and to withdraw gas at a suitable level through the pipe O having a control valve V. If the gas not withdrawn is added to the air to be treated, after it has rectified the liquid to be vaporized, only the small quantity of krypton carried away by the withdrawn vaporized gas will be lost. Again, if the obtention of oxygen is not aimed at at the same time as the obtention of krypton, the whole of the vaporized gas will be preferably added to the air to be treated.

The washing liquid, instead of being obtained in a condenser-vaporizer by heat exchange of the krypton-containing liquid which has been used for rectifying the air with a corresponding quantity of a gas under the necessary pressure, could also be derived from the treated air itself. To this effect the air may be circulated under the necessary pressure in a bundle of tubes for progressive liquefaction with backward return which is outwardly cooled by the vaporization, under a lower pressure, of the greater part of the liquid resulting from the backward return and to which the small quantity of the necessary make-up liquid has been added. The krypton accumulates in the small nonvaporized part which is withdrawn from the backward return apparatus. In the same way the air may be passed into a rectification column surmounted at its top by a condenser-vaporizer which is outwardly fed by the liquid which has been used for the rectification. The greater part of the liquid is vaporized in the condenser-vaporizer under a suitable pressure, whereas the non-vaporized part, which is rich in krypton, is withdrawn. These both last mentioned manners of forming the washing liquid have however the drawback that they necessitate the indirect transfer of cold to the whole of the treated air through the extensive surfaces which are necessary for this cold transfer.

The process of this invention necessitates, at least for the air to be rectified, which constitutes by far the larger part of the treated gas, small pressure differences only. The air may for instance be compressed to a pressure slightly above the atmospheric and, after having been cooled, be expanded with external work, preferably in a turbine, so as to provide all or part of the make-up liquid which is necessary for carrying out the process. This liquid may also be formed in any

other known way. If the krypton-containing liquid is vaporized by means of a substantially equal quantity of a cold gas, this gas may for instance consist of the expanded part of a gas subjected to the known cycle of liquefaction under pressure, whereas the non-expanded part provides the make-up liquid. In this case a cold gas is compressed with heat exchange between the gas to be compressed and the compressed gas, and then divided into two parts; one part is expanded with production of external work to a pressure which still allows of its liquefaction within a bath of the krypton-containing liquid to be vaporized, into which it is passed; the other part flows further in heat exchange with the cold gas to be compressed, and is liquefied by contact therewith, thus providing the make-up liquid.

The appended figure diagrammatically shows by way of example a manner for carrying out the process.

Air which has not previously been freed from its carbon dioxide is passed at the surrounding temperature, under a small pressure, for instance about 1,7 atm. absolute, alternately into the two cold regenerators A1 and A2. The figure shows the flow of the air to be treated through the regenerator A1. When leaving this regenerator the air is at a temperature of about —185° C. It is expanded with production of external work to about atmospheric pressure by passing through the turbine B. When leaving the turbine its temperature amounts to about minus 199° C. It is then passed to the bottom of the rectification column C, whereas krypton-free liquid air, the quantity of which is about the tenth part of the quantity of the treated air, is discharged at the top of the column. The liquid collected at the bottom of the column is nearly wholly vaporized in the vaporizer D, which is situated beneath the column C and is heated up by the coil I.

In order to heat the vaporizer D and at the same time obtain the liquid which is used for rectifying the air, including the necessary make-up liquid, the procedure is as follows: About one tenth of the krypton-free air which leaves the column C is compressed in the compressor E to about 15 atm. and the cold air to be compressed is successively passed through the exchanger-liquefier G in counter-current to a part of the same air once compressed, then through the exchanger F in counter-current to the whole of the compressed air; that part of the compressed air which does not flow through the exchanger-liquefier G is expanded in the expansion-machine H to a pressure between 2 and 3 atm. absolute, which is sufficient for its liquefaction in the heating coil I of the vaporizer D in which it is passed; the liquid air formed in the coil I, to which the liquid air resulting from the liquefaction of that part of the compressed air which passes through the exchanger-liquefier G is added, is discharged at the top of the rectification column C. That part of the air freed from its krypton leaving the column C which is not recompressed, that is about nine tenths of this air, is passed through the regenerator A2, in which it gives up its cold.

The air could also be expanded after instead of before its rectification, immediately before entering the regenerator A2.

That small quantity of liquid which is not vaporized in the vaporizer D is discharged at the top of an auxiliary rectification column K at the bottom of which the larger part of the discharged liquid is vaporized by means of a heating coil L which is supplied with a portion of the cold compressed air which leaves the exchanger F. The liquid formed in the coil L is united with that formed in the coil I. The gas, containing some krypton, which leaves at the top of the column K is united, by means of the pipe M, with the gas which rises above the vaporizer D. The liquid which is withdrawn in a small quantity at the bottom of the column K is rich in krypton. Krypton may be extracted therefrom in a substantially pure state by physical and chemical purification performed in known manner. A pipe P having a control valve Q connects the pipe M, through which the gas boiled from the liquid in the column K is conducted to the column C, with exchanger-liquefier G so that oxygen-rich gas may be passed into the gaseous liquefaction system when it is desired to increase the oxygen content of the washing liquid introduced into the top of the column C. A suitable pump R may be included in the pipe line P in order to force the oxygen-rich gas therethrough and into the exchanger-liquefier G.

I claim:

1. In a process of obtaining krypton, the steps which comprise bringing air in a gaseous state into intimate contact with a liquefied gas more volatile than krypton to thereby wash krypton from said gaseous air and produce a liquid enriched in krypton, and removing nitrogen and the greater part of the oxygen of the gaseous air as waste gas.

2. In a process of obtaining krypton and xenon, the steps which comprise cooling gaseous air while maintaining it in a gaseous state, bringing said cooled gaseous air into intimate contact with a liquefied gas more volatile than krypton to thereby wash krypton and xenon from said cooled gaseous air and produce a liquid enriched in krypton and xenon, and removing nitrogen and the greater part of the oxygen of the cooled gaseous air as waste gas.

3. In a process of obtaining krypton, the steps which comprise cooling gaseous air down to the neighborhood of its dew point, bringing said cooled gaseous air into intimate contact with liquefied air to thereby wash krypton from said cooled gaseous air and produce a liquid enriched in krypton, and removing nitrogen and the greater part of the oxygen of the cooled gaseous air as waste gas.

4. In a process of obtaining krypton, the steps which comprise bringing air in a gaseous state into intimate contact with a liquefied gas more volatile than krypton to thereby wash krypton from said gaseous air and produce a liquid enriched in krypton, removing nitrogen and the greater part of the oxygen of the gaseous air as waste gas, and treating the obtained krypton-enriched liquid to increase the krypton content thereof.

5. In a process of obtaining krypton, the steps which comprise cooling gaseous air down to the neighborhood of its dew point, bringing said cooled gaseous air into intimate contact with a liquefied gas more volatile than krypton to thereby wash krypton from said gaseous air and produce a liquid enriched in krypton, removing nitrogen and the greater part of the oxygen of the cooled gaseous air as waste gas, and treating the obtained krypton-enriched liquid to increase the krypton content thereof.

6. In a process of obtaining krypton, the steps which comprise washing air in a gaseous state with a quantity of a liquefied gas more volatile

than krypton sufficient to retain substantially the whole of the krypton contained in said gaseous air but insufficient to retain substantially the whole of the oxygen of said gaseous air, to produce a liquid enriched in krypton.

7. In a process of obtaining krypton, the steps which comprise cooling gaseous air while maintaining it in a gaseous state, washing said cooled gaseous air with a quantity of liquefied air sufficient to retain substantially the whole of the krypton contained in said cooled gaseous air but insufficient to retain substantially the whole of the oxygen of said cooled gaseous air, to produce a liquid enriched in krypton, and treating the krypton-enriched liquid to increase the krypton content thereof.

8. In a process of obtaining krypton, the steps which comprise cooling gaseous air while maintaining it in a gaseous state, washing said cooled gaseous air with a quantity of liquefied nitrogen sufficient to retain substantially the whole of the krypton of the cooled gaseous air but insufficient to retain substantially the whole of the oxygen of the cooled gaseous air, to produce a liquid enriched in krypton.

9. In a process of obtaining krypton, the steps which comprise cooling gaseous air while maintaining it in a gaseous state, and washing said cooled gaseous air with a liquid mixture of oxygen and nitrogen which is richer than atmospheric air in oxygen to produce a liquid enriched in krypton.

10. In a process of obtaining krypton and xenon, the steps which comprise cooling atmospheric air down to the neighborhood of its dew point, washing said cooled gaseous air with a liquid mixture of oxygen and nitrogen which is richer than atmospheric air in oxygen, to thereby produce a liquid enriched in krypton and xenon, vaporizing from said krypton-and-xenon-enriched liquid constituents thereof more volatile than krypton and xenon to thereby increase the krypton and xenon content thereof.

11. In a process of obtaining krypton, the steps which comprise washing gaseous air with a liquid mixture of oxygen and nitrogen which is richer than atmospheric air in oxygen, to produce a liquid enriched in krypton, and concentrating by vaporizing and rectification the obtained krypton-enriched liquid.

12. In a process of obtaining krypton and xenon, the steps which comprise cooling gaseous air down to the neighborhood of its dew point, washing said cooled gaseous air with a quantity of a nitrogen-containing liquefied gas sufficient to retain substantially the whole of the krypton of the cooled gaseous air but insufficient to retain substantially the whole of the oxygen of the cooled gaseous air, to produce a liquid enriched in krypton and xenon, and vaporizing nearly the whole of the liquid which was used for washing the cooled gaseous air.

13. In a process of obtaining krypton, the steps which comprise bringing gaseous air into intimate contact with a liquefied gas more volatile than krypton to produce a liquid enriched in krypton, removing as waste gas nitrogen and the greater part of the oxygen of the treated gaseous air, vaporizing from said obtained krypton-enriched liquid constituents thereof more volatile than krypton, and uniting the vaporized constituents with the gaseous air to be treated.

14. In a process of obtaining krypton, the steps which comprise cooling gaseous air while maintaining it in a gaseous state, washing said cooled gaseous air with a liquefied gas more volatile than krypton to produce a krypton-enriched liquid, removing as waste gas nitrogen and the greater part of the oxygen of the treated gaseous air, and vaporizing nearly the whole of the liquid utilized for washing krypton from the treated air by heat exchange with substantially an equivalent quantity of a gas more volatile than krypton, which gas is thus liquefied and serves as a washing liquid for gaseous air to be treated.

15. In a process of obtaining krypton, the steps which comprise cooling gaseous air while maintaining it in a gaseous state, washing said cooled gaseous air with a quantity of a liquefied gas more volatile than krypton which is small in proportion to the amount of cooled gaseous air, compressing a cold gas more volatile than krypton with heat exchange of the cold gas to be compressed successively in a first stage with a part of the same gas once compressed, whereby said part is liquefied, and in a second stage with the whole of said gas once compressed, partially expanding that part of the gas once compressed which is not subjected to the first stage heat exchange, liquefying said partially expanded part of the gas by heat exchange with the liquid utilized for the washing of the treated air, whereby said liquid is nearly entirely vaporized, expanding the two liquids resulting from said liquefaction of the portions of the compressed gas, and utilizing said two liquids as washing liquid for cooled gaseous air to be treated.

16. In a process of obtaining krypton, the steps which comprise cooling gaseous air while maintaining it in a gaseous state, washing said cooled gaseous air with a liquefied gas more volatile than krypton and containing no constituents less volatile than oxygen, vaporizing nearly the whole of the liquid utilized for washing the cooled gaseous air, rectifying the gas resulting from said vaporization by the liquid to be vaporized, and withdrawing a part of the gas undergoing rectification.

17. In a process of obtaining krypton, the steps which comprise passing gaseous air and a liquefied gas more volatile than krypton in opposite directions through a chamber, discharging nitrogen mixed with the greater part of the oxygen from said chamber, collecting krypton-enriched liquid within said chamber, and treating said krypton-enriched liquid to increase the krypton content thereof.

18. In a process of obtaining krypton, the steps which comprise bringing gaseous air into intimate contact with a washing liquid at a temperature lower than the temperature of liquid oxygen at the pressure under which the washing operation is conducted, to produce a krypton-enriched liquid, removing as waste gas nitrogen mixed with the greater part of the oxygen of the gaseous air, and treating the obtained krypton-enriched liquid to increase the krypton content thereof.

19. In a process of obtaining krypton, the steps which comprise cooling gaseous air while maintaining it in a gaseous state, bringing said cooled gaseous air into intimate contact with a washing liquid at a temperature lower than the temperature of liquid oxygen at the pressure under which the washing operation is conducted, to produce a krypton-enriched liquid, removing, as waste gas, nitrogen mixed with the greater part of the oxygen of the cooled gaseous air, utilizing said waste gas, before being finally discharged, to cool incoming gaseous air, and treating the obtained

krypton-enriched liquid to increase the krypton content thereof.

20. In a process of obtaining krypton, the steps which comprise bringing gaseous air into intimate contact with a liquefied gas more volatile than krypton at a temperature lower than the temperature of liquid oxygen at the pressure under which the washing operation is conducted, to produce a liquid enriched in krypton, a part of said washing liquid being obtained by cooling a pre-compressed gaseous medium by heat exchange with said krypton-enriched liquid, removing, as waste gas, nitrogen mixed with the greater part of the oxygen of the gaseous air, utilizing said waste gas, before being finally discharged, to cool incoming gaseous air, and treating the obtained krypton–enriched liquid fraction to increase the krypton content thereof.

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