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PROCESS OF OBTAINING CONSTITUENTS OF AIR HAVING A HIGHER BOILING POINT THAN OXYGEN

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Fig.1

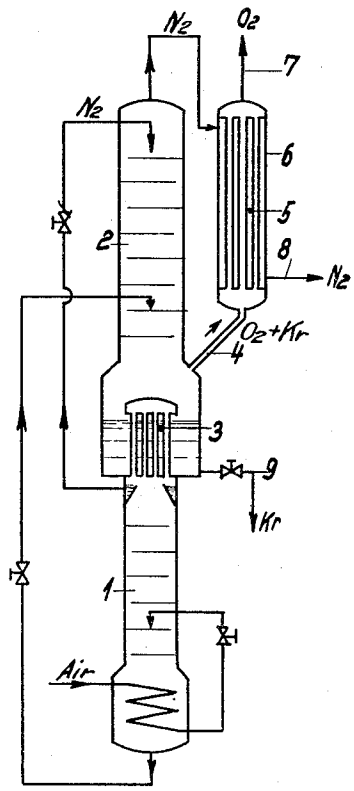
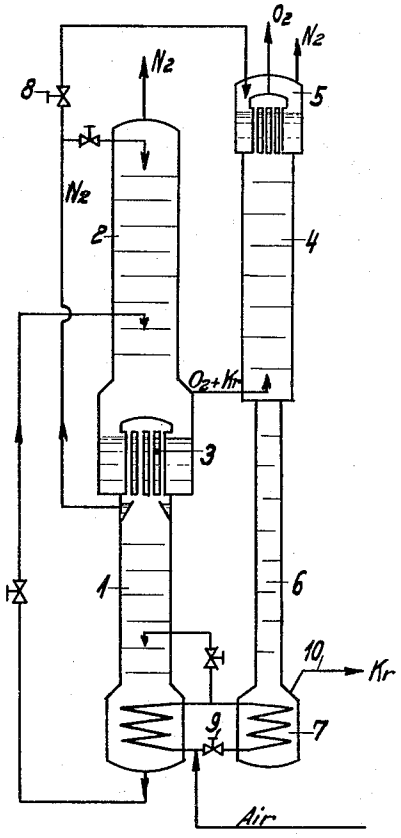


Fig.2



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PROCESS OF OBTAINING CONSTITUENTS OF AIR HAVING A HIGHER BOILING POINT THAN OXYGEN

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3 Claims. (Cl. 62—175.5)

The present invention relates to a process for obtaining constituents of air having a higher boiling point than oxygen; for example, krypton and xenon. For the sake of brevity, "krypton" will be used in the following specification and claims as representative of such higher boiling constituents.

It is known that in the separation of the constituents of air by cooling to low temperatures only a small portion of the krypton is found in the liquid oxygen remaining in the evaporator. The greater portion of the krypton is contained in the gaseous oxygen withdrawn, and in fact in about five times the concentration in which it is found in atmospheric air. It has previously been proposed to obtain the krypton from the gaseous oxygen by selective absorption in carbon or silica gel, but this method has serious disadvantages, of which only the discontinuity of the process, the relatively small adsorptive capacity of the adsorbents for krypton at its low partial pressure, and the difficult removal and working up of the absorbates will be mentioned. It has also been proposed to obtain the krypton from the liquid portion of the oxygen which remains in the evaporator of the separation apparatus. For the reasons mentioned above, a quantitative recovery of krypton cannot be obtained in this manner. Moreover, difficulties are met in the rectification of the liquid because of the rapid obstruction of the plates of the column with the solid impurities, such as ice and solid carbon dioxide contained in the liquid oxygen.

All of these disadvantages are avoided by the present invention. It has been found that the krypton can be obtained in very high concentration and yield by washing it out of the gaseous oxygen by means of krypton-free oxygen in countercurrent. This result was all the more surprising in that it appeared quite improbable that a constituent contained in a gas in the extremely low concentration of 5 parts per million could be obtained in good yields by a technical washing process.

Nevertheless, the washing out of krypton can be effected very satisfactorily when carried out in accordance with the invention, particularly if an efficient rectification column is used. A more satisfactory and uniform method of operation is obtained by using the gaseous oxygen, because this no longer contains any impurities which can seperate on the rectifier plates in solid form.

The use of a krypton-free or practically krypton-free washing liquid is essential for the successful operation of the process. The liquid nitrogen obtained in the separation of air could be used for this purpose, because it has the greatest difference in boiling point from krypton of any of the constituents of air. However, since it mingles with the separated oxygen in the washing process and therefore seriously contaminates it, krypton-free oxygen is used as the washing liquid, which is obtained by liquefying a portion of the separated oxygen by deep cooling in the upper part of the washer.

The counter-current washing of the krypton out of the gaseous oxygen is effected most simply in a vertical tube sheaf, into the lower part of which the gaseous oxygen from the evaporator of the separation apparatus flows at about its boiling temperature. The tube sheaf is suitably cooled externally, advantageously by the cold nitrogen coming from the apparatus, which in temperature and amount suffices for the formation of the necessary amount of washing liquid. The formation of the washing liquid can also be effected in a condenser located at the head of the washing column and supplied with liquid air or liquid nitrogen.

It is particularly advantageous to use an efficient rectifying column for the washing apparatus, into the lower part of which the oxygen vapor from the evaporator is supplied, while a condenser is provided at the top of the column.

The further enrichment of the washing liquid in krypton can be effected most simply by returning the washing liquid from the washer into the oxygen evaporator of the air separation apparatus. In this way the krypton becomes more and more concentrated in the liquid oxygen in the evaporator, which at the end of a period of operation may be drawn off and worked up into pure krypton.

Another method of enrichment which affords the possibility of continuously producing krypton of any desired concentration consists in passing the liquid oxygen coming from the washing column into a rectification column, advantageously situated under the washing column, and heated at its lower end. The vapors coming from this auxiliary column are returned to the lower part of the washing column. In this method of operation, in order to obtain a quantitative yield of krypton, it is advantageous at the end of a period of operation of the separation system to vaporize the liquid oxygen remaining in the evaporator into the washing column, or a small amount of liquid oxygen in the evaporator may be allowed to continuously flow

into the auxiliary column, in order to avoid the concentrating of krypton in the condenser.

The invention will be more particularly described for the purpose of illustration with reference to the accompanying drawing in which Fig. 1 is a diagrammatic representation of apparatus for carrying out one embodiment of the invention, and Fig. 2 is a diagrammatic representation of apparatus for carrying out another embodiment of the invention.

In Figure 1, 1 is the high pressure column, 2 the upper column, and 3 the evaporator and condenser of an air separating apparatus. The krypton-containing gaseous oxygen coming from the evaporator at 4 passes into the vertical tube sheaf 5. Gaseous nitrogen from the separator flows through the jacket 6 and passes out at 8. Since the nitrogen is about 13° colder than the oxygen, and in amount is about 4 times the amount of the oxygen, a copious condensation of oxygen takes place in the upper part of 5. The downwardly flowing liquid washes the krypton out of the upwardly flowing gaseous oxygen and is thereby largely revaporized and thus enriched in krypton. Since the gaseous oxygen reaching the upper end of the tube sheaf has been freed from krypton by the washing, it serves for the production of a krypton-free washing liquid by condensation. The krypton-containing washing liquid flows into evaporator 3, through 4; there a further progressive enrichment in krypton takes place. At the end of the period of operation of the separation system the liquid in the evaporator, containing substantially all of the krypton of the treated air, is drawn off at 9 and worked up into pure krypton in known manner.

In the method illustrated in Figure 2 the washing out and concentration of the krypton is effected in rectification columns. The krypton-containing gaseous oxygen from the evaporator 3 of the air separation apparatus is led into the washing column 4, which is provided with rectifying plates. The condensation of the krypton-free washing liquid takes place in condenser 5 which is cooled with liquid nitrogen supplied through valve 8. The operation of column 4 corresponds in principle with the previously described operation of tube sheaf 5 of Figure 1. The krypton-containing liquid oxygen at the bottom of the column passes into the enriching column 6 and is there further concentrated. The heating of this column is effected by means of compressed air the amount of which is regulated by valve 9. The highly concentrated krypton can be drawn off in gaseous form at 10 or can be drawn off from the evaporator 7 in liquid form. By this method of operation it is possible to obtain a continuous production of krypton of any desired concentration.

The operation of column 4 and condenser 5 will be explained in more detail by an example:

It will be assumed that 100 cubic meters of krypton-containing gaseous oxygen pass from 3 into column 4 and that this gas is in equilibrium with a liquid containing 10 times its concentration of krypton. If the liquid passing from column 4 into column 6 is to contain all of the krypton, its amount must be 10 cubic meters; that is, on the assumption of the same heat of vaporization for krypton and oxygen, 10 cubic meters of oxygen must be condensed in condenser 5.

When the system is put into operation a krypton-containing liquid will at first condense in 5, and in fact the first drops condensing will have a krypton content ten times that of the gas, corresponding to the equilibrium; in the course of further condensation, however, because of the progressive impoverishment of the gas phase in krypton, the condensate becomes poorer and poorer in krypton. On the whole, therefore, immediately after putting the system in operation the condensate will contain, it is true, some krypton, but in much lower concentration than is in equilibrium with the krypton-containing oxygen flowing up the column. In flowing down through the column this liquid must come into equilibrium with the rising vapors; that is, it must take up krypton from the vapors while vaporizing a corresponding amount of oxygen. The vapors arriving at condenser 5 thus become more and more poor in krypton than at first, and likewise the condensate therefrom. The impoverishment of the rising vapors in krypton continues until a permanent condition is finally reached wherein only krypton-free oxygen reaches the condenser, in which 10 cubic meters of krypton-free oxygen are condensed, while 10 cubic meters of a mixture of liquid oxygen with all of the krypton in the entering vapors leave the bottom of the column.

The operation of the apparatus of Figure 1 differs only from a structural point of view, the principle of operation being the same.

In a prior method krypton-containing oxygen was fed into the top of a column in liquid form. The gases drawn off had to be in equilibrium with this liquid and therefore must contain krypton, so that an appreciable part of the krypton must be lost with the vapors. On the contrary, by the process of the invention, it is possible for the first time to obtain all of the krypton contained in the air.

The concentration of krypton in the oxygen depends on the length of time the air separation apparatus is operated. In the method of operation illustrated in Fig. 1 substantially all of the krypton present in the air treated in a given period of operation will be found in the evaporator liquid. Since the amount of liquid in the evaporator is relatively large and the amount of krypton in the air is only 1:1,000,000, at the end of a normal period of operation only a small percentage of krypton will be found in the evaporator liquid. In the method of operation illustrated in Fig. 2, it is possible to further concentrate the krypton-containing oxygen by rectification in column 6, so that it is possible, after a sufficiently long period of operation, to draw off pure krypton at 10.

A further advantage of the new method is that by utilizing gaseous oxygen no obstruction of the rectifier plates by impurities is encountered, since it contains no noticeable trace of harmful impurities.

The method of the invention provides a continuous and quantitative separation of krypton from the air in heretofore unattained concentration. It can be operated with the simplest means and at very low cost. Together with the krypton, other substances having higher boiling points than oxygen are obtained, particularly xenon.

I claim:

1. An improvement in the method for obtaining krypton and xenon and other constituents of air having a higher boiling point than oxygen which comprises separating air by low temperature cooling and rectification into a low boiling portion consisting of constituents of air of lower boiling point than oxygen and a high boiling por-

tion containing substantially all of the oxygen, vaporizing oxygen from said high boiling portion, and subjecting all of the oxygen vaporized from said high boiling portion to countercurrent washing with liquid oxygen which has been freed of its krypton content by rectification.

2. An improvement in the method for obtaining krypton and xenon and other constituents of air having a higher boiling point than oxygen which comprises separating air by low temperature cooling and rectification into a low boiling portion consisting of constituents of air of lower boiling point than oxygen and a high boiling portion containing substantially all of the oxygen, vaporizing oxygen from said high boiling portion, subjecting all of the oxygen vaporized from said high boiling portion to selective liquefaction with backward return of condensate in a condenser cooled with liquid nitrogen, and returning the krypton-containing condensate to said high boiling portion.

3. An improvement in the method for obtaining krypton and xenon and other constituents of air having a higher boiling point than oxygen which comprises separating air by low temperature cooling and rectification into a low boiling portion consisting of constituents of air of lower boiling point than oxygen and a high boiling portion containing substantially all of the oxygen, vaporizing oxygen from said high boiling portion, passing all of the oxygen vaporized from said high boiling portion into the lower part of a rectification column cooled at its head with liquid nitrogen and subjecting the krypton-containing liquid from said column to rectification in a subjacent column from which the vapors pass into the upper column.

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