

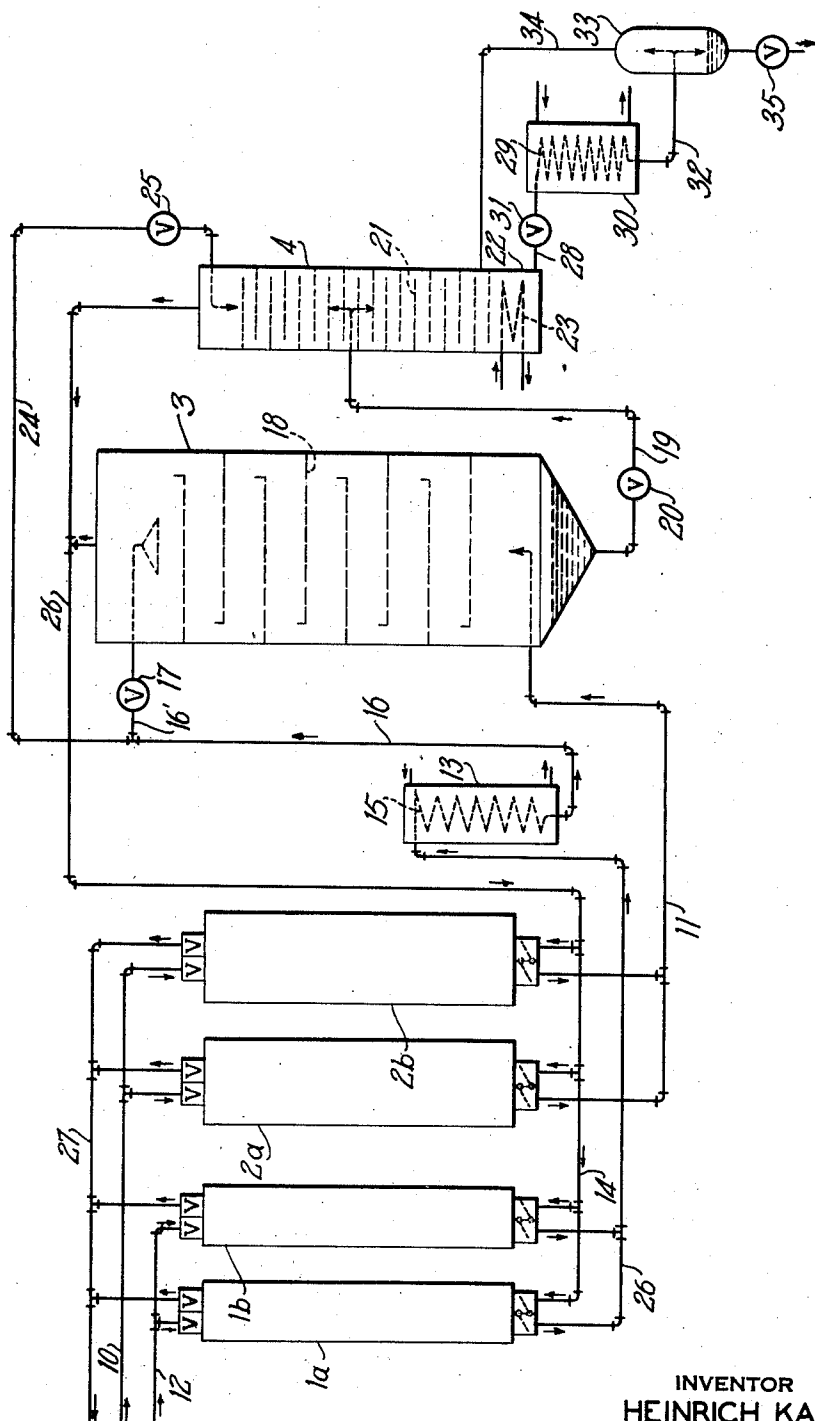
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SEPARATION OF KRYPTON AND XENON FROM AIR

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SEPARATION OF KRYPTON AND XENON
FROM AIR

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This invention relates to the separation of krypton and xenon from air and more particularly to a process of and apparatus for the production of krypton and xenon by washing air with liquid air and concentrating the krypton and xenon contained in the liquid air.

The rare gases krypton and xenon are concentrated together and hereinafter will be collectively referred to as krypton.

It is known that krypton may be produced from air by cooling the air in periodically alternated cold accumulators to approximately its dew point temperature, thereupon washing it with a small quantity of liquefied air and then again heating it in the cold accumulators. The washed liquid which has taken up the krypton is then enriched to a higher krypton content in an additional rectification column. Such procedure involves the difficulty that hydrocarbons are also washed out of the air and are enriched together with the krypton, and such hydrocarbon concentration constitutes a great explosive danger in liquid air or oxygen. A removal of all of these hydrocarbon contaminations prior to the separation of the air is not economically feasible.

Due to the simultaneous enrichment of the hydrocarbons in addition to the krypton, comparatively narrow limits are imposed upon the degree to which enrichment of the krypton in the washed liquid may safely be carried. The principal object of the present invention is to provide a simple method of operation which makes it possible, despite the presence of hydrocarbons, to carry the concentration of krypton so far in a single stage that the enriched washing liquid after removal of the hydrocarbons can be processed directly to substantially pure krypton in a single additional stage. Another object of the present invention is to provide an improved apparatus for carrying out such process.

These and other objects and advantages of this invention will become apparent from the following description and accompanying drawing, which diagrammatically illustrates an exemplary apparatus for effecting the separation of a krypton concentrate from air according to the invention.

The main volume of the air from which the krypton is to be separated, is compressed to a relatively low pressure by suitable means not shown and supplied through conduit 10 to a pair of regenerators 2a and 2b wherein it is cooled to approximately its dew point temperature in the customary manner by contact with cold surfaces in the regenerators. The air leaves the

regenerators 2a or 2b through conduit 11 and is hereupon introduced into the lower portion of column 3. Approximately 10% of the total air to be processed, after compression to a higher pressure, is supplied through conduit 12 and cooled in a pair of cold accumulators 1a or 1b, thereafter being liquefied in suitable manner, for example, in a cooler or liquefier 13. The cold air to be liquefied is conducted by conduit 14 to a coil 15 in liquefier 13 from which conduits 16 and 16' conduct the liquefied air to the upper portion of column 3. The liquefier 13 is refrigerated by a suitable low temperature medium conducted therethrough. A throttling or control valve 17 is interposed in the conduit 16' for reducing the pressure of and regulating the proportion of reflux liquid supplied to the column 3.

The column 3 is provided with suitable gas and liquid contact means such as trays 18 so that the air introduced through conduit 11 is effectively washed by the reflux liquid. Liquid containing the krypton washed out of the air collects at the bottom of column 3 and is conducted therefrom by a conduit 19 to the mid-portion of a rectifier column 4, the flow being regulated by valve 20. Column 4 is also provided with trays or perforated plates 21 and has a sump 22 at its lower end which is heated by a coil 23. The vapors produced by such heating rise in the column in countercurrent contact with the descending liquid.

In order to prevent losses of krypton, an additional portion of liquid air is introduced at the top of column 4. Such liquid is supplied by a branch 24 of conduit 16, the amount being controlled by valve 25 therein. The cold air from which the krypton has been washed is conducted from the tops of both columns 3 and 4 by conduit 26 to the cold ends of all the regenerators, alternately 1a or 1b and alternately 2a or 2b wherein it deposits refrigeration and is warmed. The air free of krypton leaves the warm ends of the regenerators through a conduit 27.

The sump 22 is connected by a conduit 28 to the upper end of an evaporator or vaporizer coil 29 in a vaporizer 30, the flow being controlled by a valve 31. The lower end of coil 29 is connected by conduit 32 to a gas and liquid separator 33 from the upper end of which the released gas flows to the lower portion of column 4 through conduit 34. The relatively pure krypton concentrate is withdrawn from the lower part of separator 33 through a conduit 35.

According to the invention, not merely the small portion of an enriched liquid intended for

further processing is to be withdrawn from the bottom of column 4, but rather an appreciably greater volume of liquid is withdrawn and a major portion thereof evaporated in the subsequent vaporizer 29 under continuous downflow of both liquid and vapor. The vapors produced are separated from the remaining liquid in separator 33 and are led back into column 4, preferably on or below the lowermost tray, for the purpose of preventing krypton losses. If in the processing of, for example, 15,000 cubic meters of air per hour it is desired to attain a thousand-fold enrichment of the krypton in the liquid, which is to be processed into pure krypton, it would be expected that no more than 15 cubic meters per hour must be withdrawn from the bottom of column 4. According to the invention, however, many times this amount, for example 80 cubic meters per hour, are withdrawn and evaporated in the evaporator 29 to a residue of 15 cubic meters per hour which is withdrawn at 35, and the thereby resultant vapors which are poor in krypton and hydrocarbons are led back from the separator 33 into the column 4.

It has been found preferable that evaporator 29 have no blind angles and opportunities for the deposition of solid removed components such as, for example, acetylene. For this purpose, for example, the liquid is evaporated in a simple tube 29 with continuous co-current downflow and the separation of the vapors is effected in a subsequent separator 33 of simple construction. The valve 31 through which the liquid is transferred from column 4 into auxiliary evaporator 29, and likewise the valve in conduit 35 through which the liquid is withdrawn from separator 33, shall be of such streamline construction that a flow is obtained which is as free from eddies and shocks as possible. Furthermore it is advisable to conduct the flow through the valves with as little pressure drop as possible in order to eliminate all danger of explosion from any solid acetylene that may have been separated.

In contrast to the otherwise customary method of operation and according to a further feature of the invention, the evaporation of the liquid in the after-evaporator is carried out with a relatively small heating surface and relatively large temperature differences. These provisions make it possible to operate with smooth tubes of simple form without division and of comparatively small volume. In order to attain the great temperature differences required during the heating of the evaporator 29, it may even be necessary to renounce the utilization of the refrigeration liberated by the evaporation and to supply the heat by external means as, for example, by circulating water at a relatively high rate through the evaporator shell 30.

The most favorable ratio for the evaporation in the after-evaporator 29 lies between 4 and 10, that is, the liquid withdrawn from column 4 is to be reduced in evaporator 29 to at least one-quarter, and at the most to one-tenth, of its original volume.

By the described process it is possible to reduce to a great extent the krypton and therewith in particular the hydrocarbon content of the liquid on the bottom of column 4, without necessarily in any way reducing the degree of enrichment in the liquid drawn off at 35 for further processing. The following advantages result:

The greatest concentration of the hydrocar-

bons is transferred from one of the main rectification columns to the small after-evaporator 29 and separator 33, that is, to a portion of the apparatus which is of relatively very small dimension. This greatly increases the safety of the main rectification. Furthermore, this appreciably reduces the volume of liquid in which the krypton is enriched to a high concentration inasmuch as the volume of the after-evaporator 29 and separator 33 in comparison to the volume of the sump 22 of column 4 are small. Finally, for example, when shutting down the plant, the processing of the liquid stored in the sump 22 of the krypton column is possible in a comparatively brief time by the auxiliary evaporator 29.

Through the method of operation according to the invention, it becomes possible to carry the enrichment of krypton in the first stage even further than heretofore inasmuch as it is permissible to approach much closer to the explosion limits with the hydrocarbon concentration in the small auxiliary evaporator 29, in which it can be easily watched and controlled, than is permissible in the large enrichment column.

While a particular embodiment of the invention has been shown, it will be apparent to those skilled in the art that modifications may be made without departing from the spirit and scope of this invention. For example, other krypton containing gases than air may be processed according to the method and with the apparatus of this invention. An example of such gas is flue gas which would result in a concentration of the residual oxygen with the krypton and hydrocarbons. By the present invention such concentration can be controlled so that it does not become dangerous. In the claims the term air is intended to include any gas resulting from air and containing krypton, the washing liquid being a liquid obtained by subjecting a portion of such gas to a liquefaction.

I claim:

1. Process for the production of krypton and xenon from air which comprises compressing and cooling air, compressing, cooling and liquefying a relatively small portion of air, washing said cooled air with a portion of the liquefied air to form a washing liquid containing krypton, rectifying said washing liquid with another portion of said liquefied air, withdrawing the rectified washing liquid at a relatively high rate, effecting rapid evaporation of a major portion of said withdrawn liquid under continuous downflow, separating the vapors of said evaporation from the remainder of the withdrawn liquid, returning said vapors to said rectification step to be rectified with additional portions of washing liquid, and withdrawing from said separation the remainder of the liquid containing a relatively high concentration of krypton.

2. Apparatus for separating krypton and xenon from air comprising means for cooling air compressed to a suitable pressure, means for washing such cooled air with liquid air, column means for rectifying the liquid product from said washing means with additional liquid air, a separate evaporator connected to receive rectified washing liquid from said rectifier column, a separator for separating liquid and vapor discharged from said evaporator, passage means for returning vapor from said separator to said rectifying column and means for continually withdrawing liquid from said separator.

3. Apparatus for separating krypton and xenon

from air comprising a pair of regenerators for alternately cooling air to be washed, a second pair of regenerators for alternately cooling a smaller volume of air, means for liquefying said smaller volume of air, means for washing said cooled air with a portion of said liquefied air, column means for rectifying a liquid withdrawn from said washing means with another portion of said liquefied air, means for heating the lower portion of said rectifier column, a separate vaporizer for rapidly but incompletely vaporizing liquid drawn from the lower portion of said rectifier, a separator for separating liquid and vapor discharged from said vaporizer, means for returning vapor from said separator to said rectifier, and means for continuously withdrawing liquid from said separator.

4. Process for the production of krypton and xenon from air which comprises cooling the air, washing such cooled air by countercurrent contact with liquid air whereby the krypton is concentrated in the washing liquid, rectifying said krypton containing washing liquid with an additional quantity of liquid air, withdrawing the rectified liquid at a relatively high rate, separately vaporizing a major portion of said withdrawn liquid, separating the vapors produced by said vaporization from the residue of the withdrawn liquid, returning said separated vapors to said rectifying step for further treatment and withdrawing said residue of liquid containing a relatively high concentrate of krypton.

5. Process for the production of krypton and xenon from air which comprises treating air at low temperatures to form a liquid containing said rare gases, subjecting such liquid to rectification to form a rare gas containing concentrate, withdrawing said concentrate from said rectification stage at a relatively high rate, separately vaporizing a major portion of said concentrate during continuous co-current downflow to a degree such that the ratio of evaporation between the volume of liquid before said evaporation and the volume of liquid remaining after said evaporation is between 4 and 10, separating the vapors produced from such remainder of liquid, returning such separated vapors to the rectifying stage, and withdrawing said remainder of liquid containing a relatively high concentration of said rare gases.

6. Process for the production of krypton and xenon from air which comprises treating air at low temperatures to form a liquid containing said rare gases, subjecting such liquid to rectifi-

cation to form a rare gas containing concentrate, withdrawing said concentrate from said rectification stage at a relatively high rate, separately and rapidly vaporizing a major portion of said concentrate by heat-exchanging contact with a relatively small heating surface heated by a relatively high-temperature heating medium whereby the quantity of liquid being subjected to evaporation at any given instant is relatively small, separating the vapors produced from the remainder of said concentrate, returning such separated vapors to the rectification stage, and withdrawing said remainder containing a high concentration of said rare gases.

7. Apparatus for separating krypton and xenon from air comprising means for cooling air compressed to a suitable pressure, means for washing such cooled air with liquid air, column means for rectifying the liquid product from said washing means with additional liquid air, a separate evaporator connected to receive rectified washing liquid from said rectifying column, said evaporator comprising a tubular heating surface having its outlet lower than its inlet and arranged so that the liquid and vapor flow therethrough is uninterruptedly downward, means for supplying a relatively high-temperature heating medium so as to externally heat said evaporator, a separator connected to receive vapor and a remainder of liquid from the outlet of said evaporator for separating such liquid from the vapor produced, passage means for returning vapor from said separator to said rectifying column, and means for withdrawing liquid from said separator.

8. Apparatus for separating krypton and xenon from air comprising means for cooling air compressed to a suitable pressure, means for washing such cooled air with liquid air, column means for rectifying the liquid product from said washing means with additional liquid air, said column having a liquid collecting space in the lower portion thereof, a separate evaporator connected to receive rectified washing liquid from said rectifier column, a separator for separating liquid and vapor discharged from said evaporator, the combined volume of said separator and said evaporator being substantially less than the volume of the liquid holding space of said rectifying column, passage means for returning vapor from said separator to said rectifying column, and means for withdrawing liquid from said separator.

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