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PROCESS AND APPARATUS FOR OBTAINING NOBLE GASES

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Fig. 1

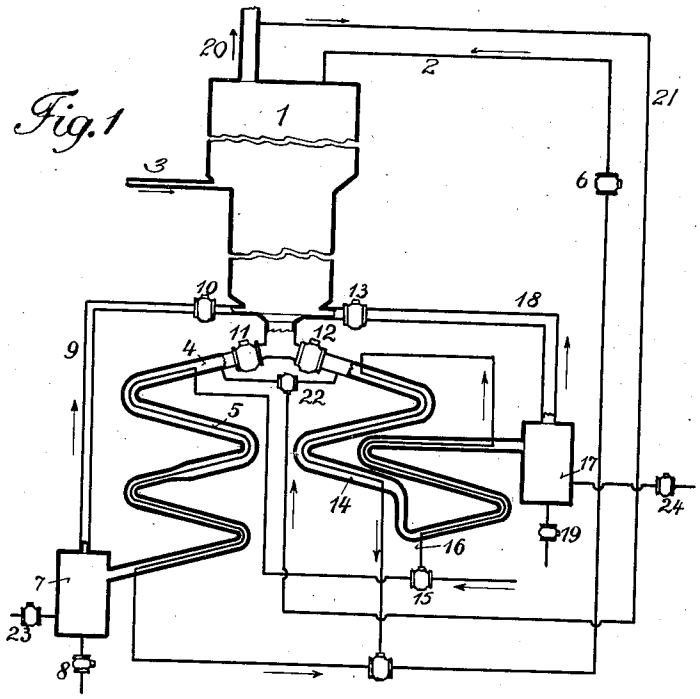
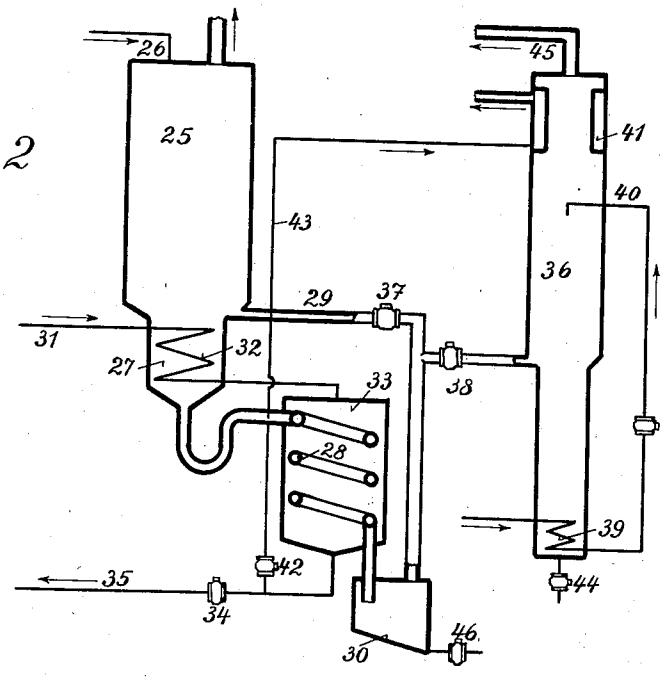


Fig. 2



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PROCESS AND APPARATUS FOR OBTAINING NOBLE GASES

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The present invention relates to a process and apparatus for obtaining, particularly from air, the noble or inert gases having boiling points higher than that of oxygen.

Rectification is often applied in the separation of the inert gases having boiling points higher than that of oxygen, particularly of krypton, from air or other suitable starting mixtures containing oxygen.

I have now found that it is advantageous to evaporate liquid oxygen, obtained for example by rectification of liquid air, or other liquefied starting mixture while said liquid flows as a continuous stream through a suitable evaporating device. I have found that undesirable by effects, such as the crystallization of hydrocarbons, particularly of acetylene, may be avoided if the evaporation of the liquefied starting material is effected while the said liquid flows as a continuous stream through a suitable evaporating device. According to this invention, liquid oxygen obtained, for example, by the rectification of liquid air is evaporated in one or several elongated stills. The stills, or evaporating devices used differ from the usual rectification column in that they have a very small cross-sectional area and are of a great length. The still may be of any desired form, for example in the form of a coil or of several coils running in parallel or of a nest of tubes. The vapor produced by this simple evaporation process necessarily contains a relatively large quantity of the inert gases. In order to continue rectification and increase the separation of inert gases from the vaporized oxygen it is advisable to recirculate the vaporized oxygen through the initial rectification column or to further treat the vapors in another column. By this method the concentration of inert gases and of hydrocarbons in the residual liquid may be considerably increased without endangering the work. Furthermore large losses of inert gases are avoided inasmuch as the quantity of liquid drawn from the still can be kept very low. This is possible because a still which corresponds with the description given is continuously well rinsed and fresh liquid continuously flows through the various sections. Furthermore, dilution of the residual liquid by fresh or partially evaporated liquid does not occur readily. The residual liquid oxygen discharged from the still is of a relatively small volume as compared to the volume of the starting material and contains a high concentration of the inert gases as well as of hydrocarbons. This produces a substantial increase in the working safety.

Inasmuch as the hydrocarbons have even higher boiling points than the inert gases, the ratio of hydrocarbons to inert gases in the residual liquid increases whereas the ratio of hydrocarbons to inert gases in the vapor produced decreases. According to this invention it is preferred to reconduct the vapor produced to the rectification column. A small quantity of hydrocarbons are thereby returned to the rectification column. The quantity of residual liquid discharged from the still must therefore be adjusted in such a manner that the quantity of hydrocarbons returned to the column will be maintained sufficiently small as to be unobjectionable. If the quantity of residual liquid discharged is small, or in any case if it is desirable, all, or part of the vapor produced may be introduced into another rectification column. In this column the krypton remaining in the vapor is washed out in the usual manner. This column may be provided with a still in accordance with the present invention or with one of the ordinary stills. The residual liquid from the first still and the liquid withdrawn from the still of the second column are further treated by any desired known chemical or physical rectification and purification process in order to obtain the inert gases in the desired purity.

In accordance with this invention, the liquid being evaporated and the vapor produced may be made to circulate in the elongated still in counter-current, in continuous current or partially in counter-current and partially in continuous current. Circulation of the liquid and vapor as a continuous current is desirable since high velocity of flow in a still of small cross sectional area is possible. If the circulation is counter-current it is advantageous to gradually decrease the cross-sectional area of the still to correspond with the gradually decreasing total quantity of liquid and vapor flowing.

It is preferable to give the stills the form of internally or externally heated coils. A liquid separator is mounted at the discharge end of the still in order to separate the liquid residue from the vapor produced.

After a still works for a long time, separations of hydrocarbons may occur on the walls of the still in spite of the thorough rinsing. In order to prevent these separations from becoming objectionable or dangerous, two stills may be mounted in parallel in order that they may be operated alternately, thereby permitting one still to be cleaned while the other is being used. In cleaning the still, the supply of liquid to the

still is cut off and heating is continued at the same or at a higher temperature. A suitable dry gas may be passed through the still during this heating operation in order to assist the removal of the separations from the walls.

The accompanying drawing illustrates the invention.

Figs. 1 and 2 diagrammatically illustrate two forms of the apparatus.

As shown in Fig. 1, the apparatus comprises a rectification column 1 into which a stream of liquid air may be introduced through pipe 2 and vaporous air may be introduced through pipe 3. Both quantities of air, or at least one of them contain the inert gases having higher boiling points than oxygen that are to be obtained. The liquid passes down through the column 1 and then passes into the still 4 as a continuous stream. The still 4 is, in comparison to the rectification column 1, of very small cross-sectional area. In view of the fact that the flow of liquid and vapor produced in still 4 is counter-current, the cross-sectional area of the still is progressively decreased to correspond roughly with the total quantity of liquid and vapor flowing through the still. The still 4 is heated by means of tube 5 through which compressed air is passed. This air is liquefied by the evaporation of the liquid in the still and is conducted through valve 6 and pipe 2 into the rectification column. A separator 7 is provided at the discharge end of still 4 to receive the discharge from the still and separate the vapor from the residual liquid. The separated vapor may be conducted back to the column by means of pipe 9 and valve 10. The liquid residue obtained and which contains the inert gases of high boiling points as well as hydrocarbons and other impurities of high boiling points is withdrawn from separator 7 by means of the valve 8.

As shown in Fig. 1, a second still 14 may be arranged in parallel with still 4. Still 14 differs from still 4 in that it provides two distillation stages, in the first of which the liquid and the vapor flow counter-current to each other and in the second stage of which the liquid and vapor flow in continuous current into separator 17. In the first stage the vapor produced flows directly back into the column whereas in the second stage the vapor is conducted into separator 17 wherein the vapor is separated from the residual liquid. The vapor is thereafter conducted back to the column 1 by means of pipe 18 and valve 13. The residual liquid is withdrawn from separator 17 by means of valve 19.

Compressed air for heating the liquid is supplied to tube 16 of still 14 through valve 15. As in still 4, this compressed air is liquefied by the evaporation of the liquid in the still and this liquefied air is then conducted through valve 6 and pipe 2 into the rectification column 1.

To effect the cleaning of the non-operating still a part of the gases leaving the column 1 at 20, is withdrawn through pipe 21 and is thereafter discharged into stills 4 or 14 by means of three-way cock valve 22.

Valves 11 and 12 are provided at the inlets of stills 4 and 14 respectively in order to control the flow of liquid to the stills. By operating stills 4 and 14 alternately the still out of operation may be cleaned of any separations before they become objectionable. Gas may be withdrawn from the separators 7 or 17 by means of valves 23 or 24 respectively.

The apparatus shown in Fig. 2 comprises a rectification column 25 into which the starting liquid is introduced through pipe 26. The starting liquid may, for example be liquid oxygen containing krypton which is obtained from a two stage air-separating apparatus, not shown. A still 27, of conventional construction may be arranged at the bottom of column 25 for forming a relatively small part of the vapor passed through column 25. The still 27 is heated by means of compressed nitrogen supplied through pipe 31 to coil 32. The greater part of the evaporation of the liquid oxygen takes place in the still 28 which is shown in the form of an elongated coil. A chamber 33 surrounds still 28 and the compressed nitrogen is conducted from the coil 32 into the chamber 33. The compressed nitrogen is liquefied by the evaporation of liquid oxygen in stills 27 and 28 and this liquefied nitrogen may be returned to said two-stage air-separating system by means of valve 34 and pipe 35. The evaporating liquid and the vapor produced flow downwardly in still 28 in a continuous current. Liquid is maintained in still 27 at a sufficient level to force evaporating liquid and vapor through still 28 into separator 30 and to reconduct separated vapor through valve 37 and pipe 29 into the column 25. The residual liquid is withdrawn from separator 30 by means of valve 46.

Instead of conducting the vapor separated at 30 back to column 25 as described above, some or all of such vapor may be conducted to a second rectification column 36 for further treatment. This may be done by closing or partially closing valve 37 and opening valve 38. The rectification column 36 is provided with a still at its bottom. This still may be heated by means of compressed air which is supplied to the heating coil 39. This compressed air is liquefied by the evaporation of liquid in the still. This liquefied air may be supplied to the air-separating device described or it may be introduced as washing liquid in column 36 by means of pipe 40, as shown in the drawing. Column 36 is provided with a condenser 41 which is charged with liquid nitrogen obtained from the chamber 33. Liquid nitrogen is withdrawn from the discharge pipe of chamber 33 through valve 42 and is conducted to the condenser 41 by means of pipe 43. Liquid oxygen containing a large proportion of inert gases is drawn off at 44. Oxygen which is freed to a large extent from the inert gases is withdrawn from column 36 through outlet 45. The liquid withdrawn at 44 and 46 is further treated in any suitable manner in order to obtain the inert gases in the desired purity.

I claim:

1. The process of obtaining noble gases having higher boiling points than oxygen which comprises supplying gaseous and liquefied mixtures containing oxygen and the said noble gases to a rectification column, passing the liquid obtained at the bottom of said column through an evaporating device as a continuous stream, vaporizing said liquid in said evaporating device, continuously passing the liquid and the produced vapors to a separator, separating vapor from the residual liquid, returning the separated vapor to the rectification column and removing this liquid from the separator.

2. The process of obtaining noble gases having higher boiling points than oxygen which comprises supplying gaseous and liquefied mixtures containing oxygen and the said noble gases to a rectification column, passing the liquid obtained at the bottom of said column from said column through an evaporating device as a continuous stream, vaporizing said stream of liquid in said

evaporating device, passing the oxygen vapor counter-current to the stream of liquid to said column, continuously passing the stream of liquid and accompanying vapors from said evaporating device to a separator, separating vapor from the residual liquid, returning the separated vapor to the rectification column and removing this liquid from the separator.

3. The process of obtaining noble gases having higher boiling points than oxygen which comprises supplying gaseous and liquefied mixtures containing oxygen and the said noble gases to a rectification column, passing the liquid obtained at the bottom of said column from said column through an evaporating device as a continuous stream, vaporizing said liquid in said evaporating device, passing the oxygen vapor produced in the first stage of the evaporation counter-current to the stream of liquid to said column, passing the vapor produced in the next stage of the evaporation with the residual liquid as a continuous current to a separator, separating vapor from the residual liquid, returning the separated vapor to the column and removing this liquid from the separator.

4. The process of obtaining noble gases having higher boiling points than oxygen which comprises supplying gaseous and liquefied mixtures containing oxygen and the said noble gases to a rectification column, passing the said liquid obtained at the bottom of said column as a continuous stream through an evaporating device as a continuous stream, vaporizing said liquid in said evaporating device, passing the vapors produced in the evaporation to a rectification column to effect a further separation of inert gases from the vapor, removing the residual liquid from the evaporating device as a continuous stream.

5. The method of obtaining noble gases having a higher boiling point than oxygen which comprises supplying air to a rectification column, passing the liquid oxygen obtained at the bottom of said column through an evaporating device as a continuous stream, supplying compressed air in heat exchanging relation to said stream of liquid oxygen and partially vaporize the same, condensing said compressed air and introducing the same into the rectification column, conducting the vapor produced in the said evaporating device to a second rectification column to effect a further separation of noble gases from said vapor.

6. An apparatus for obtaining noble gases from oxygen-containing gas mixtures which comprises a rectification column, an evaporating device of relatively small cross-sectional area and of relatively great length connected at one end with the bottom of said rectification column and a separator connected with the discharge end of said evaporating device.

7. An apparatus for obtaining noble gases from oxygen-containing gas mixtures which comprises a rectification column, an evaporating device of relatively small cross-sectional area and of relatively great length connected at one end with the bottom of said rectification column, means for supplying a continuous stream of liquefied oxygen-containing gases to said evaporating device and a separator connected to the discharge end of said evaporating device.

8. An apparatus for obtaining noble gases from oxygen-containing gas mixtures which comprises a rectification column, an evaporating device of relatively small cross-sectional area and of a relatively great length connected at one end with the bottom of said rectification column, means for supplying a continuous stream of liquefied oxygen-containing gases to said evaporating device, means for heating said stream of liquid, means for effecting a further separation of inert gases from the vapor produced and means for removing the residual liquid from the evaporating device.

9. The process of obtaining noble gases having higher boiling points than oxygen which comprises supplying gaseous and liquefied mixtures containing oxygen and the said noble gases to a rectification column, passing the liquid obtained at the bottom of said column through an evaporating device as a continuous stream, vaporizing said liquid in said evaporating device, passing the residual liquid and the vapors produced to a separator, separating vapor from liquid, passing said vapor to another rectification column to effect a further separation of inert gases from the vapor and removing the liquid from the separator on the one side and from the evaporating device of the second rectification column on the other side.

10. An apparatus for obtaining noble gases from oxygen-containing gases which comprises a rectification column, an evaporating device consisting of at least one coil of relatively great length connected at one end with the bottom of said rectification column and a separator connected with the discharge end of said evaporating device.

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