FIG. 1
PROCESS OF AND APPARATUS FOR THE PRODUCTION OF ARGON

Rudolf Becker, Munich-Solln, and Johannes Wachter, Pullach, Germany, assignors to Gesellschaft fuer Linde's Elektrohütten A. G., Hoellriegelskreuth, near Munich, Germany

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This invention relates to a process of and apparatus for the production of argon, and more particularly relates to the manufacture of nitrogen-free argon from an argon-oxygen-nitrogen mixture obtained during the two-stage rectification of air.

It is already known to produce mixtures of oxygen having a high argon content by removing the nitrogen contained in a mixture of nitrogen and oxygen in the upper column of a two-stage rectification apparatus. Thereafter, the fraction of the oxygen which contains the argon and the higher boiling fractions is reintroduced into the rectification apparatus where it is separated into a higher boiling component consisting of oxygen and into a lower boiling component consisting of an argon-oxygen mixture. This mixture may be further separated, if desired, in a further rectification column into an argon fraction having only a residue of oxygen.

However, experience has shown that the withdrawal of the argon-containing oxygen fraction from the low pressure column of the air separation apparatus affects detrimentally the further separation of the air. Accordingly, it has been proposed to improve the known process and to prevent interference with the separation of the air by withdrawing only a portion of the oxygen-argon mixture at a higher point in the rectification apparatus where the concentration of the oxygen amounts to between 90 and 98 per cent. While this known process interferes with the air separation process less than the first process, it is still not satisfactory because only a small portion of the argon contained in air can be recovered.

It is accordingly the principal object of the present invention to provide an improved process of and apparatus for the production of argon from air whereby the major portion of the argon which is contained in the air may be recovered.

A further object of the invention is to provide a process of and apparatus for the manufacture of argon from a mixture of gases obtained during the two-stage rectification of air which will not substantially disturb the rectification of air.

In accordance with the process of the invention it is possible to recover the major part of the argon content of the air contained in the air separation column by withdrawing an argon-oxygen-nitrogen fraction at a point in a low pressure column where oxygen and nitrogen are practically comparable or equal concentration. Thereafter, the nitrogen is completely removed by rectification of the argon-oxygen-nitrogen fraction in a distillation column and by separating the remaining argon-oxygen mixture in a separation column into pure oxygen and pure argon. The rectification is carried so far in the distillation column that, for example, the argon-oxygen mixture evaporated at the bottom of the column contains only approximately 0.02 per cent of nitrogen. On the other hand, it is also possible to reduce the concentration of the argon leaving the column with the vaporized nitrogen to a minimum by using a distillation column of ample dimensions. By means of the process of the invention the argon contained in the air treated in the air separator is recovered as pure argon with a yield of about 60 per cent which is about twice the yield obtained in known processes. In some cases, it may be desirable to remove the oxygen from the argon-oxygen mixture by a known chemical method.

In a preferred modification of the process of the invention the liquid oxygen fraction obtained in the separation column is utilized to produce the sprinkling liquid required for the distillation column. The sprinkling liquid is obtained by indirect heat exchange with the nitrogen fraction condensing in the condenser coils. The evaporated oxygen is then discharged in counter-current heat exchange with fresh gas. It is also feasible to combine the two columns in a single column of the type used in air separators. In this case the sump liquid of the upper column condenses the rising nitrogen fraction of the distillation column. However, in order to limit the height of the apparatus and to reduce the cold losses the two columns are preferably disposed adjacent to each other and the sump liquid of the separation column consisting of liquid oxygen, is delivered by a pump to the condenser of the distillation column.

In order that the operation of the air separator may not be affected in any way, the cold required for the separation is produced, in accordance with the invention, by the expansion of highly compressed nitrogen which is guided in a closed circuit. This is effected as follows. At first the heat developed during the compression of the highly compressed nitrogen is dissipated. Then the nitrogen is pre-cooled in counter-current heat exchange with the expanded cold nitrogen whereafter the sump liquid of the distillation column is heated by the pre-cooled nitrogen which is thus liquefied. After further cooling in heat exchange with the oxygen evaporating in the sump of the distillation column, the liquefied nitrogen is expanded and delivered to the head of the condenser to produce sprinkling liquid from the argon fraction contained in the separating column. There the nitrogen is evaporated in indirect heat exchange with the argon fraction which condenses partially. The vaporized nitrogen is then permitted to escape and is used for further cooling of the liquefied nitrogen under pressure before it is expanded.

The apparatus for carrying out the process of the invention consists of two rectification columns which may, for example, be provided with rectification plates. One of the columns serves as a distillation column for the nitrogen to be first removed while the other column is the separation column for the argon-oxygen mixture. The apparatus further includes a liquid pump for delivering the sump liquid of the separation column (oxygen) to the condenser of the distillation column, a counter-current heat exchanger for the nitrogen cooling circuit, a counter-current heat exchanger for the separation products with the crude mixture and associated vapor.

For a better understanding of the invention reference is now made to the accompanying drawings, in which:

Fig. 1 is a schematic diagram illustrating apparatus for carrying out the process of the invention; and

Fig. 2 is a schematic diagram illustrating further apparatus for carrying out a modified process in accordance with the invention.

The argon containing mixture to be separated contains substantially equal parts of nitrogen and oxygen and is withdrawn from the low pressure column of an air separator not shown in the drawing. This mixture is introduced into a counter-current heat exchanger 1 at a pressure of about 7 atmospheres where it is cooled.

The mixture then passes through coil 6 and is introduced substantially in the center 7 of the distillation column 2. Here the mixture is separated into a nitro-
gen-free oxygen-argon fraction which collects in liquid form 3 at the bottom of the distillation column and into a nitrogen fraction containing argon and oxygen residues. The latter fraction leaves the head of the distillation column at 5, is expanded by valve 25 and reheated substantially to the temperature of the high-pressure nitrogen which enters the system. The heating takes place by heat-exchange with high-pressure nitrogen in nitrogen counter-current heat exchanger 8 or in the counter-current heat exchanger 1. A portion of the fraction may, if desired, be directed through the counter-current heat exchanger 1 in a direction opposite to that in which the crude or untreated argon mixture flows. Another portion of this fraction has previously been condensed in the coils of condenser 4 and serves as spraying liquid for the distillation column 2. The oxygen-argon fraction is withdrawn at 9 from the distillation column 2 and is first expanded by valve 10 and then introduced at 24 substantially at the center of the separation column 11. Here, the fraction is separated into an oxygen fraction which collects at the bottom of the column at 12 and into an argon fraction which is removed at 14 as pure argon and is passed through the heat exchanger 1 before being utilized. A portion of the argon vapors arriving at the head of column 11 is condensed in the coils 13 of the condenser 27 and serves as spraying liquid for the separation column. The liquid refluxed 12 of the separation column 11 is delivered by pump 15 having a motor 16 to the head of the distillation column 2 where it is evaporated in indirect heat exchange with condensing nitrogen. The evaporated oxygen is partly discharged at 21, passed through the crude gas counter-current heat exchanger 1 and heated to approximately room temperature while another part is discharged at 22 and introduced at 23 into the separation column.

The high-pressure nitrogen which serves for producing the required cold is passed after pre-cooling in the nitrogen counter-current heat exchanger 8, through coil 17 where it is liquefied. After further cooling in the liquid oxygen by passing through coil 18 and through super-cooling heat exchanger 19 the nitrogen is then passed through expansion valve 20 into condenser 27 of the separation column 11. The nitrogen evaporated in the chamber 27 in heat exchange with the argon condensing in tubes 13 is returned into the closed circuit through super-cooling heat exchanger 19 and through nitrogen-counter-current heat exchanger 8.

In accordance with a modification of the process of the invention the cold required for the separation process is produced by a closed crude argon circuit in which the crude argon mixture to be separated is also introduced and from which it is removed in a compressed state, and by means of highly compressed air. Both gases first serve in a condensed pre-cooled state to heat the separation column whereby they are liquefied. After the thus formed liquid is expanded to vaporization pressure it is employed to cool the upper part of the column whereby it is simultaneously evaporated. The vapors thus produced are brought into counter-current heat exchange with compressed air to be pre-cooled or with circulating crude or untreated argon thereby to utilize their cold content. The compressed air, however, is only used to heat the sum liquid of the distillation column and is thereby liquefied. Thereafter, the liquid is expanded and delivered to the head of the distillation column for pumping purposes.

The modified separation process of the invention will now be described by way of example with reference to Fig. 2.

The crude or untreated argon to be separated which contains besides argon approximately equal parts of oxygen and nitrogen is introduced at 31 into a closed crude argon circuit. The mixture is compressed in compressor 32 with a circulating gas to about 4 atmospheres pressure above atmospheric pressure. Thereafter, it is cooled by water cooler 33, pre-cooled in counter-current heat exchanger 34 and liquefied by the pump liquid 35 of the separation column 36 in the coil 46. A portion of the liquid thus formed is expanded by valve 37, vaporized by vaporizing coil 38 at the head of separation column 36 and returned into the circuit through counter-current heat exchangers 60 and 34. Another portion of the untreated argon mixture is introduced in liquid form into the distillation column 39 through valve 40 for the purpose of removing the nitrogen by rectification. The nitrogen driven off is discharged into the atmosphere with the vaporized fraction of the liquid air introduced at 44 through valve 62 and the outlet 65 of counter-current heat exchanger 63.

The distillation column 39 is heated and vapors are formed from the sump liquid 42 by a portion of the high pressure air which is condensed after pre-cooling in the counter-current heat exchangers 63 and 56 in exchange with escaping oxygen or nitrogen in the coil 41 in the liquid oxygen-argon mixture. The liquefied air is expanded through valves 43 and 44 and introduced into distillation column 39 at 45. Here, the liquid air trickles over the vapors rising over the rectification plates of the distillation column 39 and washes the argon and oxygen content thereof. The nitrogen fraction of the liquid air is preferably evaporated and escapes through valve 62 while a considerable part of its argon content remains in the liquid phase and is thus recovered. The liquid air to be introduced at 45 into distillation column 39 is super-cooled in heat exchanger 60 by cold crude argon.

Another portion of the highly compressed air is used for the purpose of heating the separation column in a coil 47 in addition to compressed crude argon which condenses in coil 46. After liquefaction of the air in coil 47, the air is expanded by valves 48 and 49 and evaporated in special condenser pipes 52 at the head of separation column 36. This air is thereby utilized to condense the pure argon fraction to be recovered. The vaporized air is guided in the heat exchanger 63 in counter current with a portion of the condensed high-pressure air introduced at 64 and distributed to the two counter-current heat exchangers 56 and 65.

The oxygen-argon mixture obtained by rectification is withdrawn in liquid form at 51 from the bottom of the distillation column 39 and introduced at 54 through expansion valve 53 into separation column 36 for further rectification. The oxygen component which collects in liquid form at the bottom of separation column 36 after rectification of the oxygen-argon mixture introduced therein, is first vaporized, then is discharged in gaseous form at 55 and is brought into counter-current heat exchange with highly compressed air in the counter-current exchanger 56 and is discharged through outlet 66. In order to produce in the separation column 36 simultaneously both argon of high purity as well as oxygen of high purity a portion of the rising argon-containing oxygen is continuously withdrawn in gaseous form from the separation column a few rectification plates above the level of the sump liquid. This fraction is branched off at 57 and introduced through valve 58 into the expanded circulating argon at 63.

The pure argon produced at the head of separation column 36 is withdrawn in liquid form at 59 and vaporization of the accumulated liquid argon may take place under pressure by suitable hot vaporizers, not shown, and discharged into suitable storage tanks, not shown. The liquid may also be compressed to high pressure by pumps. By excluding mechanical vaporizers and by utilizing a closed evaporation circuit any contact with other liquids, such as lubricants and the like, and any contamination by other vapors or gases can be prevented. By the process of the invention highly purified, absolutely dry gas can be directly produced.

The second process of the invention affords among
others the advantage that a large portion of the argon content of the highly compressed air utilized for the generation of cold is recovered during the process.

According to a further modification of the invention it may be expedient to omit separation columns 11 (in Fig. 1) or 36 (in Fig. 2). In this case the oxygen may be removed from the argon-oxygen mixture chemically in a known manner instead of removing the oxygen in the separation column.

The invention has been described with reference to a preferred embodiment and it will be understood that many variations and modifications thereof may be resorted to without departing from the scope of the invention as defined in the following claims.

We claim:

1. A process for the production of argon comprising the steps of withdrawing an argon-rich argon-oxygen-nitrogen fraction at a predetermined point of a two-stage air rectification process, the oxygen and nitrogen content of said fraction of gases being of substantially equal magnitude, rectifying said argon-oxygen-nitrogen fraction to remove the nitrogen substantially completely therefrom, separating the remaining argon-oxygen mixture into substantially pure argon and substantially pure oxygen by the application of cold, pre-cooling compressed air and circulating it in a circuit, expanding the pre-cooled compressed air in order to produce the required cold, indirectly cooling a portion of said argon-oxygen mixture by the expanded pre-cooled air, heating the separated substantially pure oxygen by the pre-cooled compressed air, washing out the argon from said argon-oxygen-nitrogen fraction by means of the expanded pre-cooled air, and discharging the air resulting from the washing out of the argon into the atmosphere in heat exchange with the compressed air.

2. A process as defined in claim 1 wherein oxygen containing a small portion of argon is removed in gaseous form during the argon-oxygen separation and fed into the crude argon circuit, thereby to recover simultaneously argon and oxygen of high purity.

3. A process as defined in claim 1 wherein the produced pure argon is withdrawn in liquid form, and is then vaporized under pressure.

4. A process for the recovery of argon from an argon oxygen nitrogen mixture comprising withdrawing a gaseous argon rich oxygen nitrogen fraction from an air rectification device where the oxygen and the nitrogen content is of substantially the same magnitude, rectifying the said argon oxygen nitrogen fraction to effect a complete removal of the nitrogen and thereafter separating the remaining argon oxygen mixture into its pure components, producing the cold required for the separation of the gas mixture by expansion of compressed circuit-conducted precooled crude argon and of precooled compressed air, while utilizing each of said compressed gases for heating the separating column, thereby condensing said gases and using the same upon expansion from the fluid state for the indirect cooling of the upper portion of the separating column, heating the fluid contained in the sump portion of the distillation column by compressed air only, introducing the condensed air upon expansion into the upper portion of the distillation column for rinsing and washing argon, returning the vaporized crude argon upon cold exchange in counter-current heat exchanger into the circuit and releasing the vaporized air while conducting the same in heat exchange with compressed air.

5. In an apparatus for the recovery of argon from an argon-rich oxygen-nitrogen mixture containing substantially equal parts of oxygen and nitrogen, a distillation column for the distillation of nitrogen, a separation column for separating oxygen and argon from said mixture of gases, means connecting said two columns for providing mutual cooperation thereof, a compressor and a cooler disposed in series to compress and cool the initial gas mixture, a pair of counter-current heat exchangers for pre-cooling compressed air in heat exchange counter-current flow with expanded nitrogen obtained from said distillation column and with vaporized oxygen obtained from said separation column, a further counter-current heat exchanger connected downstream of said cooler for further cooling the initial gas mixture in a heat exchange counter-current flow with argon containing oxygen derived from said separation column, a first heating coil disposed in the sump of said distillation column and connected to said pair of heat exchangers to receive pre-cooled compressed air therefrom, a second and a third heating coil superposed in the sump of said separation column to heat the latter, said second coil being connected to said pair of heat exchangers to receive pre-cooled compressed air therefrom, said third coil being connected to said further heat exchanger to receive the cooled initial gas mixture therefrom, a fourth and a fifth vaporizing coil located at the top of said separation column to vaporize the liquefied gas mixture therein, said fourth coil having its output connected to one of said pair of heat exchangers to convey cooled air thereto flowing together with said expanded nitrogen, said fifth vaporizing coil being connected to the output of said third coil for circulating a portion of the initial gas mixture.

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