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SYSTEM FOR SEPARATION OF ARGON FROM AIR

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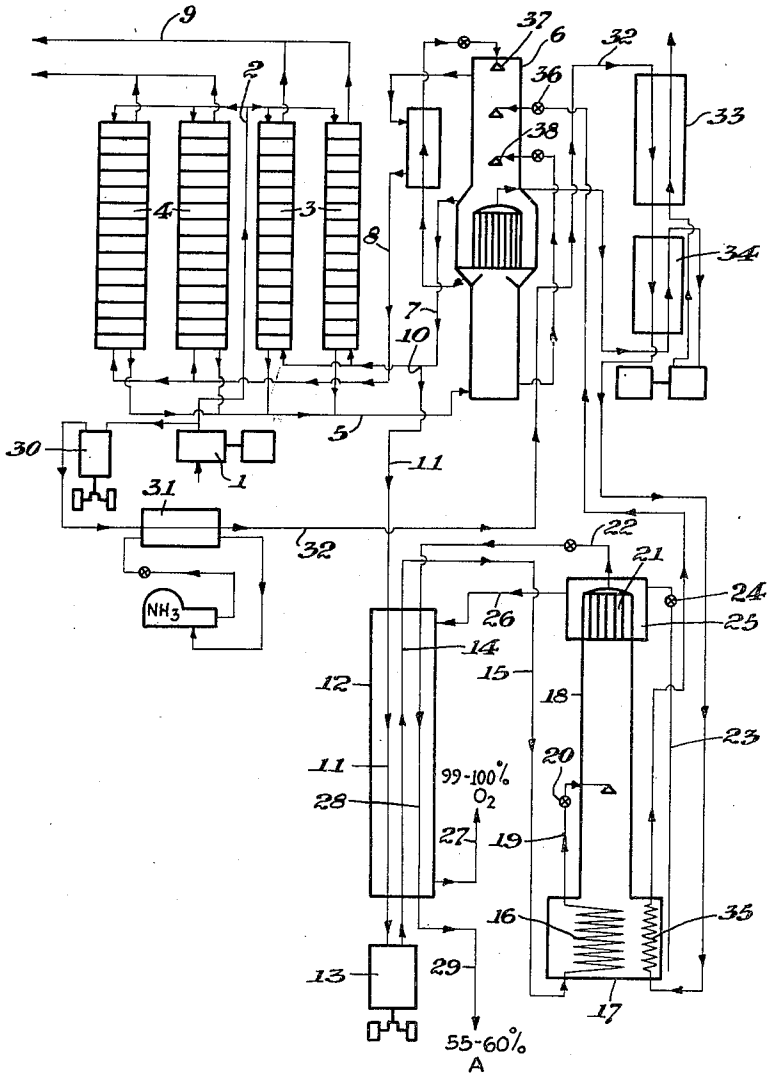

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SYSTEM FOR SEPARATION OF ARGON FROM AIR

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1

The present invention relates to improvements in the production of argon. More particularly, the invention relates to improvements in procedure and apparatus by which concentrates high in argon are obtained, especially in the well-known Linde-Fränkl systems, and to methods of operating such or other apparatus in which cold accumulators are employed for separating the constituents of air.

In the Linde-Fränkl process for producing a nitrogen fraction and an oxygen fraction, air is compressed in a turbine compressor and cooled in two pairs of accumulators, one pair of which is fed with a previously separated nitrogen fraction and the other pair with a previously separated oxygen fraction. The incoming air thus cooled is separated in a double column of the ordinary Linde type to obtain these fractions. The oxygen fraction, in normal operation, contains only about 90 to 95% oxygen and the balance is principally argon. To obtain a mixture rich in argon, the oxygen fraction is ordinarily subjected to further rectification, and the heat interchange for effecting this rectification has, prior to the present invention, been obtained primarily by means of a cycle either of nitrogen, or of argon.

The present invention incidentally makes available, on a commercial scale, oxygen of over 99% in purity, while also advantageously utilizing this as a medium for producing a desired reflux for separation of a fraction of high argon content. To accomplish this during the operation of a Linde-Fränkl air separation process, for instance, a small proportion of the separated oxygen is diverted from the stream passing to the oxygen accumulators and is subjected to certain liquefaction and rectification treatments whereby oxygen of 99% or 99.5% purity or higher is obtained, while provision is made for compensating for imbalance in the accumulators. The oxygen, thus kept uniformly high in purity serves in the course of rectification as the aforesaid medium.

By way of illustration, one method and means of carrying out the invention will be described hereinbelow with reference to the accompanying diagrammatic drawing.

The drawing illustrates the application of the invention to a Linde-Fränkl plant in which a compressor 1 for incoming air is connected by a pipe 2 to the warm ends of two pairs, 3 and 4, of cold accumulators. The air from the cold ends of the accumulators is fed through a pipe 5 to be separated in the usual manner as in a double

2

rectifying column 6 of the Linde type. Separated oxygen passes from the column 6 through a pipe 7 to the accumulators 3. Separated nitrogen passes from the column 6 through a pipe 8 to the accumulators 4. The oxygen product usually containing about 88 to 95% of oxygen and a certain proportion of argon is ordinarily drawn from the warm ends of the accumulators 3 through a pipe.

To obtain an argon product of relatively high purity by means of the present invention, cold 88%–95% oxygen at its saturation temperature is withdrawn from the above Linde-Fränkl system at 10 through a pipe 11 adjacent the cold ends of the accumulators 3, and is treated as follows: The withdrawn oxygen fraction is passed through a heat exchanger 12 to a compressor 13, where its pressure is raised to within the approximate range of 5 to 10 atmospheres absolute, and then passed back through a pipe 14 of the heat exchanger 12 and onward through a pipe 15 to a coil 16 in a kettle 17 at the base of a column 18. The 88–95% O_2, now in the form of a liquid in coil 16, is delivered through a pipe 19 and a valve 20 into the column 18. This column has about 25 plates and the point of input of the crude argon mixture is at an intermediate level therein or approximately half-way between both ends thereof, depending upon the exact percent of oxygen in the mixture, and is expanded to a column pressure of about 4 atmospheres absolute. The point of input of an 82–95% O_2, for instance, is preferably slightly below the middle point of the column 18.

In the column 18, oxygen, originally supplied from the column 6, is rectified to a liquid containing 99 or 99.5 to 99.8 or substantially 100% oxygen which collects in the kettle 17, and to gas mixture containing the desired argon which escapes from a reflux condenser 21 through a pipe 22. To obtain the desired reflux, the condenser 21 is cooled by liquid oxygen at 1.5 atmospheres absolute drawn from the kettle 17 and delivered through a pipe 23 and valve 24. Due to the difference in pressure between the inside of the condenser 21 and that in the space 25 outside of the condenser, the cold liquid 99%–100% O_2 which is boiling in this space at about 1.5 atmospheres absolute is sufficient to condense argon inside the condenser 21, thereby furnishing the desired reflux for column 18.

The evaporated O_2 from the space 25 flows through a pipe 26 to the heat exchanger 12 in contact with the pipes therein and emerges through a pipe 27, while the argon concentrate

passes from pipe 22 through a pipe 28 of the heat exchanger 12 and emerges through a pipe 29. The argon concentrate contains about 55% to 60% argon, about 35% to 40% oxygen and about 4% to 5% nitrogen.

The oxygen product is kept uniformly high in oxygen and is supplied continuously to obtain the desired continuous refluxing action in the column 18. This is to a great extent made possible by providing for the correction of imbalance in the Fränkl accumulators of systems like that described wherein the quantity of cold gases caused to leave the accumulators is or becomes less than the quantity entering the same for their subsequent fractionation.

During the operation of the apparatus shown and in the manner described, in order to compensate for the imbalance imposed upon the accumulators by withdrawal of the oxygen at point 10 of the Linde-Fränkl system, a quantity of air is added by means of an auxiliary compressor 30 sufficient to compensate for the withdrawn oxygen. Thus, if 10% of the oxygen product at point 10 is withdrawn for rectification, an equivalent quantity of additional air is introduced at the compressor 30. If desired, this oxygen withdrawal and air introduction may be automatically controlled.

The additional air introduced at the compressor 30 is preferably over and above the volumetric addition of air made in the ordinary operation of the Linde-Fränkl system, and made ordinarily to correct for thermal imbalance of the accumulators and to allow added volume of N_2 plus O_2 backward through the accumulators and to effect more perfect evaporation of impurities frozen out from the warm air entering in the opposite direction.

Air from the compressor 30 is cooled with ammonia in a heat exchanger 31 primarily to dehydrate the air. This air is passed through a pipe 32; successively through heat exchangers 33 and 34 ordinarily provided in a Linde-Fränkl system; and then through a coil 35 in the kettle 17 to supply the extra heat required to evaporate nitrogen, argon and a portion of the oxygen therein. From the coil 35, the air is expanded through a valve 36 and introduced into the upper column of the Linde double column 6 at a level preferably between the levels of the usual sprays 37 and 38, respectively for the nitrogen and low-pressure air from the lower column.

Under certain conditions the oxygen product used as a medium for producing the desired reflux in column 18 may be less than the purity indicated. When of lesser purity the pressure inside the column for rectification purposes is lower than that specifically indicated above.

The invention hereinabove set forth is embodied in particular form and manner but may be variously embodied within the scope of the claims hereinafter made.

What is claimed is:

1. A process of separating argon from air, which process comprises refrigerating air at elevated pressures in cold accumulators cooled to relatively low temperature, rectifying the refrigerated air into its major constituents including an oxygen fraction containing argon and a nitrogen fraction, separately withdrawing said fractions and cooling said accumulators therewith while diverting a portion of said oxygen fraction passing to said accumulators, liquefying said diverted portion of said oxygen fraction and rectifying said liquefied portion to a liquid oxygen residue and an overhead fraction containing argon while subjecting the separated argon in a rectifying zone to the reflux produced by continuous indirect heat exchange between the said separated argon and said liquid oxygen residue and while correcting for imbalance in the accumulators by steps comprising the following: compressing an amount of air equivalent to the amount of the said diverted portion of said oxygen fraction, cooling the said latter air in heat exchange relationship with cold separated nitrogen in the first-mentioned rectifying step, passing said latter cooled air into heat exchange relationship with the said liquid oxygen residue obtained in the second-mentioned rectifying step and supplying the so treated latter air to the first-mentioned rectifying step for fractionation with the first-mentioned air.

2. A process of separating argon from air, which process comprises refrigerating air at elevated pressures in cold accumulators cooled to relatively low temperature, rectifying the refrigerated air into a nitrogen fraction and an oxygen fraction containing argon and substantially 88–95% oxygen, separately withdrawing said fractions and cooling said accumulators therewith while diverting a portion of said oxygen fraction passing to said accumulators, liquefying said diverted portion of said oxygen fraction and rectifying said liquefied portion to a liquid residue of 99% O_2 or above and an overhead fraction containing argon while subjecting the separated argon in a rectifying zone to the reflux produced by continuous indirect heat exchange between the said separated argon and said liquid oxygen residue and while correcting for imbalance in the accumulators by steps comprising the following: compressing an amount of air equivalent to the amount of the said diverted portion of said oxygen fraction, cooling the said latter air in heat exchange relationship with cold separated nitrogen in the first-mentioned rectifying step, passing said latter cooled air into heat exchange relationship with the said liquid oxygen residue obtained in the second-mentioned rectifying step and supplying the so treated latter air to the first-mentioned rectifying step for fractionation with the first-mentioned air.

3. A process of separating argon from air, which process comprises refrigerating air at elevated pressures in cold accumulators cooled to relatively low temperature, rectifying the refrigerated air into a nitrogen fraction and an oxygen fraction containing argon and substantially 88–95% oxygen, separately withdrawing said fractions and cooling said accumulators therewith while diverting a portion of said oxygen fraction passing to said accumulators, compressing said diverted portion of said oxygen fraction to a pressure in the approximate range of 5 to 10 atmospheres absolute, cooling the compressed diverted portion to liquefy it, introducing the liquefied diverted portion at an intermediate level in a rectification zone and expanding it therein to a pressure of approximately 4 atmospheres absolute, rectifying said latter expanded portion in said zone to an overhead fraction containing argon and to a liquid residue containing 99 to 100% oxygen while conducting said liquid residue into indirect heat-exchange relationship with the upper end of said rectification zone and while permitting said liquid residue to vaporize in such relationship at a reduced pressure of about 1.5 atmospheres absolute and subjecting said zone to the reflux action thereby produced, and while correcting for imbalance in

the accumulators by steps comprising the following: compressing an amount of air equivalent to the amount of the said diverted portion of said oxygen fraction, cooling the said latter air in heat exchange relationship with cold separated nitrogen in the first-mentioned rectifying step, passing said latter cooled air into heat exchange relationship with the said liquid oxygen residue obtained in the second-mentioned rectifying step and supplying the so treated latter air to the first-mentioned rectifying step for fractionation with the first-mentioned air.

4. A process of separating argon from air, which process comprises refrigerating air at elevated pressures in cold accumulators cooled to relatively low temperature, rectifying the refrigerated air into its major constituents including an oxygen fraction containing argon and a nitrogen fraction, separately withdrawing said fractions and cooling said accumulators therewith while diverting a portion of said oxygen fraction passing to said accumulators, liquefying said diverted portion of said oxygen fraction and rectifying said liquefied portion to a liquid oxygen residue and an overhead fraction containing argon while subjecting the separated argon in a rectifying zone to the reflux produced by continuous indirect heat exchange between the said separated argon and said liquid oxygen residue and while adding cold compressed air to the first-mentioned rectifying step to correct for imbalance in the accumulators and in a quantity equivalent to the quantity of the said diverted portion of said oxygen fraction.

5. A process of separating argon from air, which process comprises refrigerating air at elevated pressures in cold accumulators cooled to relatively low temperature, rectifying the refrigerated air into a nitrogen fraction and an oxygen fraction containing argon and substantially 88–95% oxygen, separately withdrawing said fractions and cooling said accumulators therewith while diverting a portion of said oxygen fraction passing to said accumulators, compressing said diverted portion of said oxygen fraction to a pressure in the approximate range of 5 to 10 atmospheres absolute, cooling the compressed diverted portion to liquefy it, introducing the liquefied diverted portion at an intermediate level in a rectification zone and expanding it therein to a pressure of approximately 4 atmospheres absolute, rectifying the thus expanded portion in said zone to an overhead fraction containing argon and to a liquid residue containing 99 to 100% oxygen while conducting said liquid residue into indirect heat-exchange relationship with the upper end of said rectification zone and while permitting said liquid residue to vaporize in such relationship at a reduced pressure of about 1.5 atmospheres absolute and subjecting said zone to the reflux action thereby produced, and while adding cold compressed air to the first-mentioned rectifying step to correct for imbalance in the accumulators and in a quantity equivalent to the quantity of the said diverted portion of said oxygen fraction.

6. A process of separating argon from air, introducing at an intermediate level in a rectification zone a liquid fraction of air containing argon and a major proportion of oxygen, rectifying said fraction in said zone to an overhead fraction containing argon and to a liquid residue containing 99 to 100% oxygen while conducting said liquid residue into indirect heat-exchange relationship with the upper end of said rectification zone and subjecting said zone to the reflux action thereby produced, continuing the introduction at said intermediate level in said rectification zone of said liquid fraction of air supplied from a system employing steps comprising: refrigerating air at elevated pressure in cold accumulators cooled to relatively low temperature, rectifying the refrigerated air into its major constituents including a fraction containing argon and a major proportion of oxygen, and a fraction containing primarily nitrogen, separately withdrawing said latter two fractions and cooling said accumulators therewith while diverting a portion of said fraction containing argon and a major proportion of oxygen prior to introduction of the latter fraction into said accumulators, liquefying said diverted portion, the thus liquefied portion being the first-named liquid fraction of air for introduction into said first named rectification zone; while supplying said portion, adding air in the rectification of said refrigerated air to correct for imbalance in the accumulators and in a quantity equivalent to the quantity of the said diverted portion of said fraction of air to be rectified; and withdrawing argon concentrate from the upper end of the said rectification zone.

7. In a process of separating argon from air, compressing a fraction of air containing argon and substantially 88 to substantially 95% oxygen to a pressure in the approximate range of 5 to 10 atmospheres absolute, and cooling said fraction to liquid form, introducing the liquid fraction at an intermediate level in a rectification zone and expanding it therein to a pressure of approximately 4 atmospheres absolute, rectifying said fraction in said zone to a gaseous fraction containing argon and to a liquid residue containing 99 to 100% oxygen while conducting said liquid residue maintained substantially entirely in liquid state directly into an enclosure in the upper end of said rectification zone in indirect heat-exchange relationship with the said gaseous fraction and while permitting said liquid residue to vaporize in such relationship at a reduced pressure of about 1.5 atmospheres absolute and subjecting said zone to the reflux action thereby produced; and withdrawing an argon concentrate as an overhead product from said upper end of said rectification zone.

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