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PROCESS OF SEPARATING AIR AND SIMILAR GASEOUS MIXTURES BY LIQUEFACTION AND RECTIFICATION

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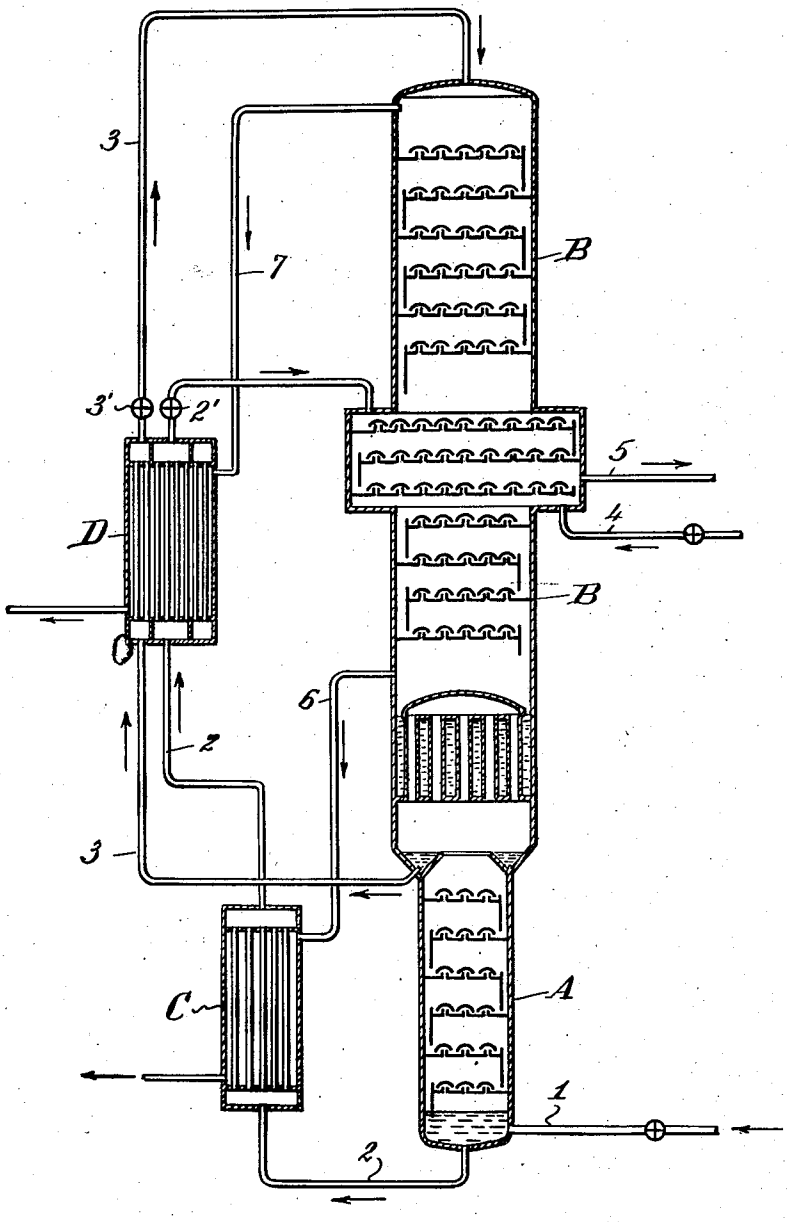

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PROCESS OF SEPARATING AIR AND SIMILAR GASEOUS MIXTURES BY LIQUEFACTION AND RECTIFICATION

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This invention relates to the separation by liquefaction and rectification of gaseous mixtures, comprising at least three constituents one of which occurs in a quantity substantially less than each of the first two, and has a condensing temperature located between those of the first two. The process therefore applies particularly to atmospheric air in which argon occurs in a substantially smaller quantity than either oxygen or nitrogen, and its condensing temperature is located between these last two gases. For greater simplicity, we shall refer in the following treatise only to atmospheric air. But, it is understood that the process which will be described can be applied in a general way to gaseous mixtures of similar composition, such as were defined above.

It is common practice to separate air into oxygen and nitrogen by introducing it in the gaseous state, after having been cooled, into an intermediate level of a rectifier the lower portion of which is heated and in the upper portion of which liquid nitrogen is admitted. But in the carrying out of this process for separating air, the quantity of air that can be separated into oxygen substantially free from nitrogen and nitrogen substantially free from oxygen is smaller than that which we should be able to separate in view of the composition of the liquid mixture of oxygen and nitrogen, which contains very little argon, in equilibrium with gaseous atmospheric air. The reason is that argon accumulates in the column according to the process pointed out in U. S. Patent No. 1,068,219 of Claude. Owing to this accumulation of argon, the liquid and the gas in the column are, at the level at which the air is introduced, not binary mixtures of oxygen and nitrogen, but ternary mixtures of oxygen, nitrogen and a very substantial proportion of argon. For such ternary mixtures the ratio of the proportion of oxygen contained in the liquid to the proportion of oxygen contained in the gas is not so great as it would be if there were no argon. It has been suggested in the above noted U. S. Patent No. 1,068,219, to provide a special outlet for argon at a level immediately above one of the trays of the lower part of the rectifier column for withdrawing some gaseous oxygen rich in argon. By applying the process of this U. S. patent to the process of separating the air into its constituents by the introduction of air at an intermediate level of the rectifier, we should effectively prevent the presence of substantial quantities of argon in the column at the place of the introduction of the treated air, and we could therefore introduce into the rectifier an excess quantity of air substantially as great as if the treated air were devoid of argon. On the other hand, a fair proportion of the oxygen contained in the treated air would be recovered not as substantially pure oxygen, but as a mixture of oxygen, argon and a certain proportion of nitrogen which would have to be subjected to a new treatment, for example the one described in the U. S. Patent No. 1,638,005 of Le Rouge if we wish to obtain the oxygen in substantially pure state. Consequently in this case also, the liquid nitrogen admitted at the top of the rectifier would not enable us to separate into oxygen substantially free from nitrogen and into nitrogen substantially free from oxygen that quantity of air which (in view of the composition of that liquid mixture of oxygen and nitrogen, containing very little argon, which is in phase equilibrium with gaseous atmospheric air) should be rectified by the reflux liquid nitrogen.

To sum up, whether one does not eliminate the argon from the rectifier column by a special outlet, or whether one eliminates it by the process of the U. S. Patent No. 1,068,219, the presence of argon in the treated air has at all events the result of increasing the amount of liquid nitrogen necessary to obtain a definite quantity of oxygen substantially free from nitrogen. This liquid nitrogen is obtained by compressing nitrogen to sufficient pressure to permit liquefaction in a bath of a liquid less volatile than itself, generally the liquid oxygen from the bottom of the rectifier column. The existence of argon in the air therefore entails the disadvantage in the well known above mentioned processes, of increasing the energy necessary for the separation of the treated air.

It is the object of the invention to avoid the difficulties mentioned and to provide a simple and effective process for separating the gaseous mixture into oxygen and nitrogen practically pure.

According to the present invention, the process consists in introducing into the column a quantity of air in excess of the quantity which, (in view of the respective compositions of the air and the liquid mixture of oxygen and nitrogen in phase equilibrium therewith) might be rectified by the quantity of liquid nitrogen admitted at the top of the column and in withdrawing from the column at the level of, or a level somewhat above the place where the air is introduced, a quantity of gas richer in argon than the air and in amount substantially equal to that excess air.

The respective argon contents of the liquid

and of the gas of the column both decrease in proportion as we move upwardly from the level of air introduction. As a result, in order to lower to a determined value the argon content of the vapor of the column at the level where the air is introduced, we must withdraw all the more gas and introduce a corresponding excess of air so much the greater as the point of withdrawal is more remote from the place where the air is introduced. But the introduction and withdrawal of air in excess require a certain expenditure of energy, even if the column is at atmospheric pressure, and furtherfore the recovery of the withdrawn cold is necessarily imperfect. For these various reasons it will be advantageous to withdraw the gas enriched in argon at a place which will be as near as possible the place where the air is introduced and will only be separated therefrom, for example, by one or two rectifier trays. The gas enriched in argon can be withdrawn even at the level of the introduction of the treated air, that is, between those two rectifier trays between which the entrance for air introduction is located. In this latter case, the inlet orifice and the outlet orifice naturally must be far removed from one another but so as still to permit good mixing of the air which enters with the gas of the column.

If the withdrawal orifice of the gas enriched in argon is very close to the air entrance orifice the argon content of the gas of the column can be made as near the argon content of the air as desired, that is, about 1%. To this end, it will be sufficient to introduce into the column a sufficiently substantial excess of air. As, however, the use of an excess of air costs somewhat in cold and energy, its quantity can remain in practice, for example, between one-third and one-fifth of the sum total of the air treated by the apparatus.

The process according to the present invention is particularly applicable when the rectifier column is the low pressure column functioning at atmospheric pressure of a rectifier apparatus with both high and low pressure. In this twofold rectification the quantity of liquid nitrogen at one's command for the low pressure rectification is theoretically overabundant so that it seems that one ought to be able to introduce a considerable quantity of air into the low pressure column, without ceasing to obtain practically pure oxygen and nitrogen. But in practice the quantity of air which one thus can blow in is far lower than the theoretically calculated quantity when we consider the air as a binary mixture of oxygen and nitrogen. This is attributable to the presence of argon in the column which tends to cause the oxygen contents of the liquid and of the vapor in the column to approach each other as has been explained before. If we introduce in accordance with the present invention a quantity of air greater than that the rectification of which is theoretically possible and withdraw gas at the level or very nearly the level of introduction, for example, above the tray situated right above this orifice, the difference between the quantity of air introduced and that of the withdrawn air, i. e., the quantity of gaseous air really separated into its constituents as a supplement of the air introduced into the high pressure column, is considerably greater than that which one could advantageously introduce without withdrawal.

The liquid which is in equilibrium with the air introduced into the high pressure column and which we deliver to the low pressure column is at this low pressure in equilibrium with gas poorer in oxygen than air so that the introduction of air into the low pressure column must take place slightly below the place where the liquid rich in oxygen is admitted. To withdraw a gas having an oxygen content as close as possible to that of air, one must effect the withdrawal of the gas from the low pressure column preferably between the place of air introduction and the place where the liquid rich in oxygen is delivered.

In the accompanying drawing, the figure shows schematically the application of the process in the case of rectification of the air with high and low pressure.

In this figure, A denotes the column under pressure and B the column at atmospheric pressure. 2.72 m^3 of compressed and cold air under a pressure of between 4 and 5 atmospheres absolute is admitted through the pipe 1 at the lower portion of the column A. At the bottom of column A one collects a liquid containing about 40% oxygen, the quantity of which corresponds to 1.43 m^3 of gas and which is conducted through pipe 2 and expansion cock 2' into column B. At the top of column A one collects a quantity of liquid nitrogen which corresponds to 1.29 m^3 of gas, and conducts it through pipe 3 and expansion cock 3' to the top of column B. Through pipe 4 one blows into column B at a point situated three or four rectification trays below the place where the liquid rich in oxygen is admitted, 3.63 m^3 of cold air at atmospheric pressure. Through pipe 5 one withdraws right above the first rectification tray situated above the inlet for blowing in air 1.59 m^3 of a gas having practically the same content as the air in oxygen and nitrogen, but richer than air in argon. At the lower part and at the upper part of column B, one withdraws respectively 1 m^3 of pure gaseous oxygen by pipe 6 and 3.76 m^3 of pure gaseous nitrogen through pipe 7. The gaseous oxygen is used for sub-cooling in exchanger C the liquid rich in oxygen drawn up through the pipe 2. Likewise, the gaseous nitrogen is used to cool in the exchanger D the liquid nitrogen drawn up through the pipe 3 and the liquid rich in oxygen which was previously cooled in the exchanger C.

The process according to the present invention is independent of the processes used for the recovery of the cold of the gases leaving the rectifier column or for the creation of the cold intended to compensate the losses of cold. In case it is desired to obtain very pure oxygen and nitrogen, one will advantageously employ temperature exchangers, preferably to regenerators with alternating action, for the recovery of the cold. To facilitate the drying of the treated air and the exchange of temperature between the two gases circulating in the exchanger, it will then be advantageous to compress the air at a pressure higher than that which prevails in the column, and after passing into the exchanger to expand at least part thereof with outside work to the pressure which prevails in the column for the production of cold.

Various changes may be made in the process and apparatus as described without departing from the invention or sacrificing any of the advantages thereof.

I claim:

1. A process for obtaining substantially pure oxygen and nitrogen from atmospheric air by liquefaction and rectification, comprising withdrawing a gaseous mixture of oxygen and nitrogen rich in argon from an intermediate level of

rectification and introducing unseparated atmospheric air at substantially the same level and in quantity substantially greater than that of the gaseous mixture withdrawn.

2. A process for obtaining substantially pure oxygen and nitrogen from atmospheric air by liquefaction and rectification, comprising withdrawing a gaseous mixture rich in argon from an intermediate level of rectification and replacing said gaseous mixture withdrawn with air, introduced at substantially the same level, and in quantity substantially greater than that of the gaseous mixture withdrawn.

3. A process for separating the constituents of a ternary gaseous mixture, one constituent being present in relatively small amount and having a boiling point between those of the other constituents by liquefaction and rectification, comprising withdrawing a gaseous mixture containing a relatively large amount of the constituent having an intermediate boiling point at an intermediate level of rectification and introducing at substantially the same level of rectification a mixture of the gases containing a relatively smaller amount of the constituent having the intermediate boiling point and in quantity greater than that of the gaseous mixture withdrawn.

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