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J. WUCHERER ET AL METHOD FOR FRACTIONATING AIR BY LIQUEFACTION AND RECTIFICATION Original Filed Jan. 2, 1953

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#### METHOD FOR FRACTIONATING AIR BY LIQUE-FACTION AND RECTIFICATION

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5 Claims. (Cl. 62-175.5)

The present invention relates to an improved method and means for fractionating air by liquefaction and recti- 20 a relatively large portion of the total air-about 35% to fication.

The present application is a division of our copending application Serial No. 329,378, filed January 2, 1953 now Patent No. 2,712,738.

The oxygen obtained from atmospheric air in conven- 25 tional systems is usually without pressure. There are many cases, however, in which the oxygen is required at an increased pressure and must be compressed after it has been separated. Compression cannot be effected in conventional, lubricated compressors, requiring special 30 measures which make it desirable that the oxygen be obtained already at an increased pressure.

A method has been proposed for obtaining oxygen by liquefaction and rectification of air. In this method the rectifying column is operated at normal pressure, the 35 separated oxygen being compressed in liquid state and thereupon evaporated and heated to the ambient temperature by heat exchange with air to be fractionated. Thereby, the oxygen can be evaporated under pressure and its cold can be recovered by heat exchange with air 40 whose pressure is so high that it is liquefied at a temperature which is higher than the evaporation temperature of the oxygen. This method involves undesired losses. In order to avoid loss of cold, the difference between the temperature of the air and that of the oxygen must be 45 still greater than those of the process without a nitrogen small at the warm end of the heat exchanger. The air must be warmer than the oxygen at each point of the heat exchanger to effect heat exchange. Except at the warm end, the temperature difference is smallest at the point of the heat exchanger where the oxygen begins to evaporate. Considering the smallest permissible temperature difference at the warm end of the heat exchanger and at the point where evaporation of the oxygen begins and considering the velocity of the flowing media as well as the size of the heat exchange surfaces, the amount of air can 55 be calculated which must exchange heat with a given quantity of oxygen. If the amounts of air at a given pressure of the oxygen, are plotted in relation to increasing air pressures, the curve will have a flat minimum; the amount of air condensed during the heat exchange with 60 the oxgyen is always greater than the amount of oxygen; at the aforementioned minimum, the amount of air is in most cases 15% to 30% greater than the amount of oxygen.

Since the total amount of the substances leaving the 65 plant is equal to the amount of air which enters the plant, the amount of air which exchanges heat with the nitrogen is always smaller than the amount of nitrogen leaving the plant, increasing loss of cold. The conditions are more favorable in regenerators usually employed for the 70 heat exchange between air and nitrogen, the pressure of the air being about equal to that in the prefractionating

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column, i. e., 5 to 6 atmospheres absolute. These heat exchangers are subject to similar limitations with respect to the relative amounts of the heat exchanging gases as the oxygen heat exchanger; in these cases, however, the amount of air may be somewhat-up to 2.5%-smaller than the amount of nitrogen; if the difference is greater, the heat exchange is impaired, causing additional cold loss. If 20 parts of oxygen are obtained by the decomposition of 100 parts of air,  $20 \times 1.25 = 25$  parts of air must exchange heat with the oxygen. This leaves only 75 parts of air for exchanging heat with 80 parts of nitrogen, whereas  $80 \times 0.975 = 78$  parts of air would be required. Economic operation is therefore not possible.

Economic operation can be effected only by increasing the pressure of a part of the total amount of air, whereby the specific heat is increased and heat can be exchanged with a greater amount of nitrogen and the aforementioned gap can be closed.

This solution of the problem, however, requires that 55%-must be compressed, which required additional energy. It is not advisable to use regenerators or similar self-cleaning heat exchangers for highly compressed air, because the air remaining and lost in these devices at every reversal of flow is too great. If counterflow heat exchangers are used, the relatively great amount of air must be dried and the carbon dioxide must be separated therefrom, involving additional cost.

It has been proposed to increase the pressure of the total amount of air only to that pressure at which it is fractionated and to employ a nitrogen cycle in which the pressure of the nitrogen is increased and the latter exchanges heat with the oxygen evaporating at increased pressure. In this way drying and separation of CO<sub>2</sub> can be avoided, if the low pressure air heat exchangers (regenerators) are so constructed that a certain amount of nitrogen does not contact the heat exchange surfaces which are coated with water ice and solid carbon dioxide, the diverted nitrogen being conducted to the compressor of the cycle. However, the aforementioned difficulties of the heat exchange for air are greater for nitrogen so that an additional heat exchange, cycle-nitrogen and expanded nitrogen, must be provided. The power requirements of the conventional process employing a nitrogen cycle are cycle.

It is an object of the present invention to provide an improved method for fractionating air by liquefaction and rectification which method avoids the difficulties involved in the aforedescribed conventional methods.

It has been explained supra that there is an optimal pressure for the heat exchange between air and oxygen, at which pressure a minimum of excess air is required. This pressure is about 28 atmospheres absolute at a pressure of the oxygen of 12 atmospheres absolute and it is about 80 atmospheres absolute at a pressure of the oxygen of 25 atmospheres absolute. There is also an optimal air pressure for the unavoidable heat exchange between highly compressed air and nitrogen having no pressure, this optimal pressure being much higher than that for the heat exchange between air and oxygen. The reason for this difference is that in the case of heat exchange between air and oxygen the mean specific heat of the air must be as great as possible over a wide temperature range, because not only the sensitive heat but also the heat of evaporation must be removed from the oxygen, whereas in the case of the heat exchange between air and nitrogen, in which merely a gas must be heated, the specific heat of the air at the temperature of the environment must be as great as possible.

In the process according to the invention a mean pressure is employed for the heat exchange between air and

oxygen, which pressure depends on that of the oxygen, and a relatively small amount of highly compressed air, for example at 200 atmospheres absolute, is used in addition to a relatively great amount of air compressed to 5 to 6 atmospheres above atmospheric pressure, for the heat exchange with nitrogen, the amount of high compressed air being just sufficient to make up for the deficiency of air which would otherwise exist. If the pressure of the oxygen is 25 atmospheres absolute, 53% of the air would have to be compressed to 80 atmospheres 10 absolute, if no additional highly compressed air is used. If a portion of the air is highly compressed for the heat exchange with oxygen of 25 atmospheres absolute, only 24% of the air need be compressed to 80 atmospheres absolute and 2.5% would have to be compressed to 200 15 atmospheres absolute. The energy required in the second case is 23% less than in the first case.

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Considerable savings can also be obtained, if the ideas underlying the present invention are applied to the closed cycle system, in which a gas is circulated whose thermodynamic characteristics, particularly vapor pressure and heat of evaporation, are similar to those of oxygen and which gas can be compressed in compressors lubricated by oil. Such a gas is argon. Its boiling point is at a pressure of 760 mm. at 87.5° Kelvin (oxygen 90.2° Kelvin) and its heat of evaporation is 1500 kg.-cal./mole (oxygen 1595 kg.-cal./mole). Its only disadvantage seems to be its much lower specific heat of 5.00 kg.cal./° C. mole (oxygen 7.01 kg.-cal./°C. mole). Argon, however, must be compressed substantially less than nitro- 30 gen. If the pressure of the oxygen is 25 atm. absolute, the pressure of argon need by only 33 atm. absolute whereas the pressure of nitrogen must be 100 atm. absolute. About the same excess amount of compressed argon is required for heat exchange with oxygen as excess air 35 would be needed, if air were used for the heat exchange; this is primarily due to the low specific heat of the argon. However, because of this low specific heat, there is no deficiency, if heat is exchanged between expanded argon and air, because 7 parts argon can absorb the heat of only 5 parts air at 5.5 atm. absolute. The disadvantage is that one must employ a closed cycle, which, in contradistinction to nitrogen, does not take part in the rectification process, requiring additional heat exchange surfaces for the evaporation of the liquefied argon. Argon, however, can be obtained without difficulty as a by-product when fractionating the air so that losses due to leakage in the closed cycle can be continuously replaced.

A better understanding of the invention will be afforded by the following detailed description considered in con- 50 oxygen from the air. junction with the accompanying drawing, the one figure of which is a diagrammatic illustration of a system according to the invention, in which parts unessential to the process according to the invention are omitted.

Referring more particularly to the drawing, the air 55 tion into the closed cycle. to be fractionated is compressed in a turbocompressor 11 and conducted into one of two regenerators 12 and 12' and therefrom into the rectifying apparatus 14 after it has been cooled and conducted through an argon evaporator 13 which will be described later. The nitrogen, separated  $_{60}$ in the rectifying apparatus 14, is conducted to the other of the regenerators 12 and 12'. In each regenerator a pipe coil is provided through which argon of a pressure of about 2 atm. absolute and coming from the evaporator 13 is conducted. This avoids passage of argon through  $_6$ channels which have previously received water and separated carbon dioxide. The argon, after it has been heated to ambient temperature in the regenerators, is compressed in a compressor 15 to 33 atm. absolute and

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thereupon conducted into a heat exchanger 16 in which it is cooled and liquefied. Thereupon it is expanded in a valve 17 and returned to the evaporator 13 where it is evaporated and where it liquefies a part of the air coming from one of the regenerators. The oxygen separated in the device 14 is compressed by a pump 18 and evaporated and heated by heat exchange with compressed argon in the heat exchanger 16.

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For replenishing the circuit and replacing argon losses, a small argon separating column 19 is provided whose product passes through the heat exchanger 16 and is compressed in a small auxiliary compressor 20 and passed into an accumulator 21. From the latter so much argon is passed into the argon circuit through a reducing valve 22 as is needed to replace losses. The accumulator 21 may

be omitted, if desired. Since the amount of argon circulating in the closed circuit is smaller than the amount of nitrogen in a nitrogen circuit at approximately the same compression ratio, the 20 power requirements are considerably less than those of a nitrogen circuit and are not much greater than when producing oxygen without pressure and subsequent compression of the oxygen. The amount of argon circulating in the circuit is in the order of 24% of the amount of air 25 to be decomposed, whereas the amount of nitrogen circulating in the nitrogen cycle would be 33%.

What is claimed is:

1. A process for fractionating air comprising the steps of compressing the air to be fractionated, indirectly cooling and thereby liquefying at least a part of the air by indirect heat exchange with evaporating argon, separating the oxygen in the air in a rectifier, compressing the separated liquid oxygen, evaporating and heating the compressed oxygen to ambient temperature by indirect heat exchange with argon circulating in one closed circuit in which the argon is compressed, the compressed argon being cooled and liquefied by the aforesaid indirect heat exchange with the compressed liquid and evaporating oxygen, the compressed and cooled argon being expanded 40and evaporated by the aforesaid heat exchange with the compressed air prior to the compression of the argon.

2. A process as defined in claim 1 in which the compressed air is supplementally cooled in regenerators whose cold storage masses are periodically cooled by nitrogen separated from the air in the rectifier. 45

3. A process as defined in claim 1 in which argon lost from the closed argon circuit is replaced by argon separated from the compressed and cooled air by rectification supplementally to the rectification for separating the

4. A process according to claim 3, the supplementally separated argon being heated by heat exchange with oxygen, which has been separated from the air, and the argon being compressed and expanded prior to introduc-

5. A process according to claim 3, the supplementally separated argon being heated by heat exchange with the separated oxygen, compressed, accumulated, and expanded prior to introduction into the closed cycle.

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