Sept. 3, 1963 J. V. FETTERMAN 3,102,801

LOW TEMPERATURE PROCESS

Filed Jan. 24, 1957 4 Sheets-Sheet 1

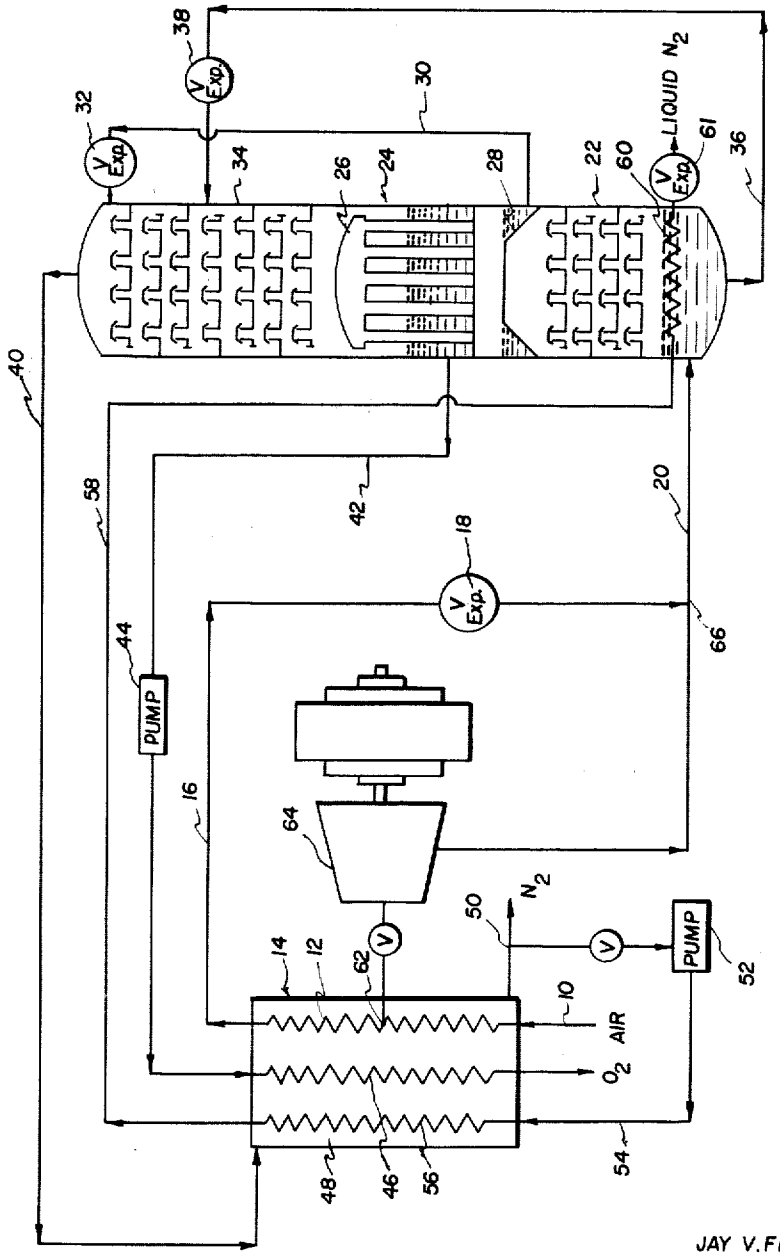



FIG. 1

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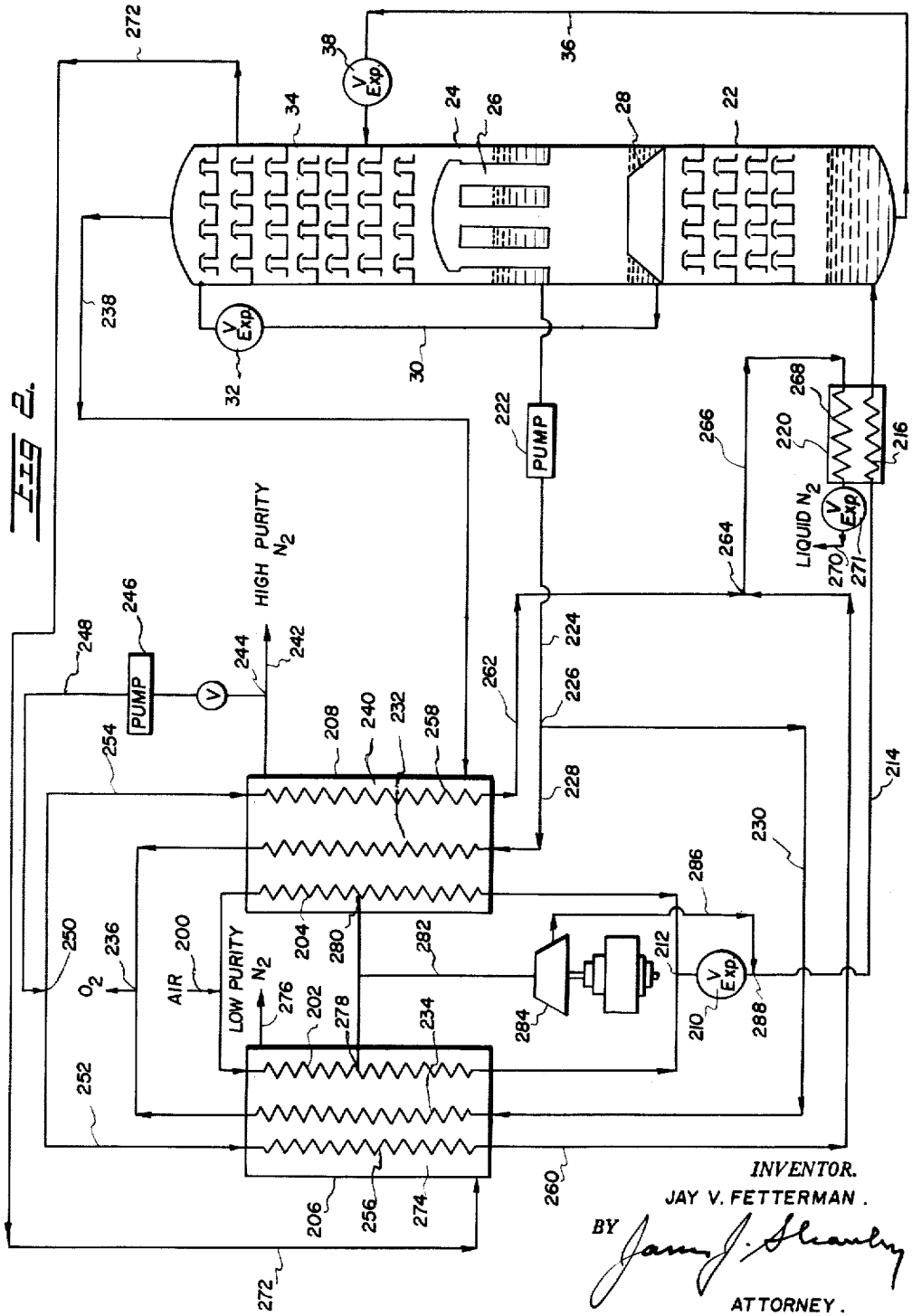
ATTORNEY.

Sept. 3, 1963 J. V. FETTERMAN 3,102,801

LOW TEMPERATURE PROCESS

Filed Jan. 24, 1957 4 Sheets-Sheet 2

Fig 2.



Sept. 3, 1963 J. V. FETTERMAN 3,102,801

LOW TEMPERATURE PROCESS

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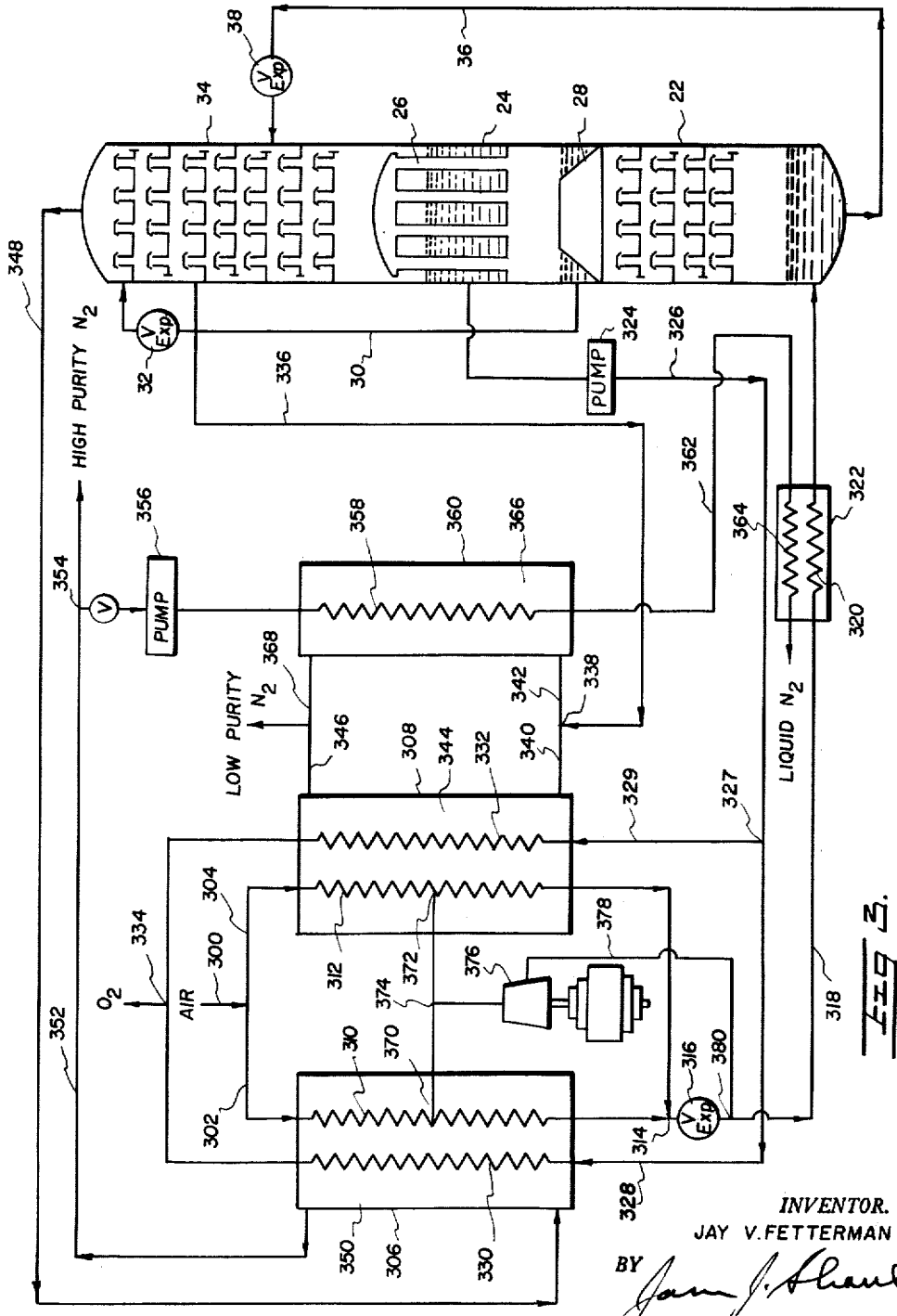



FIG 2.

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Sept. 3, 1963 J. V. FETTERMAN 3,102,801

LOW TEMPERATURE PROCESS

Filed Jan. 24, 1957 4 Sheets-Sheet 4

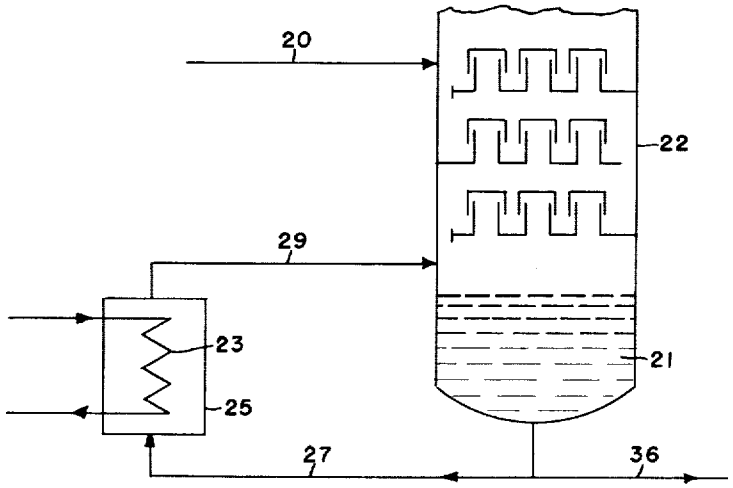



Fig. 4

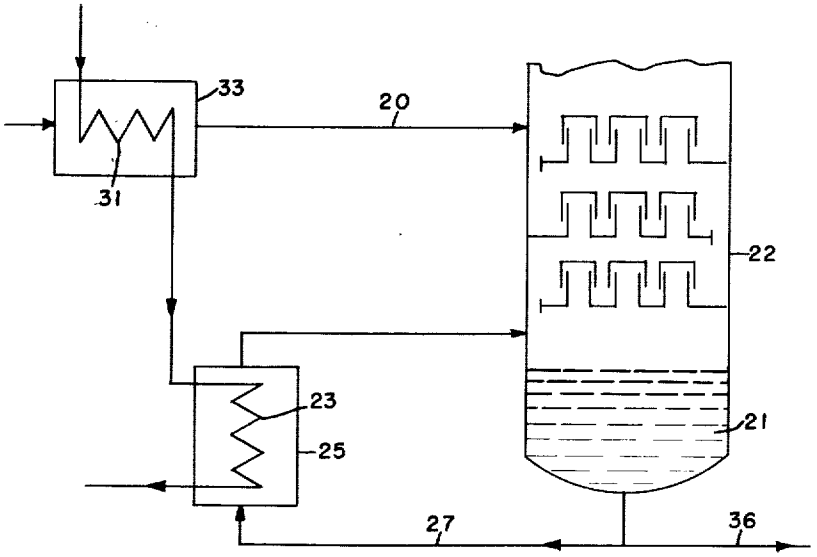



Fig. 5

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United States Patent Office 3,102,801 Patented Sept. 3, 1963



3,102,801

# LOW TEMPERATURE PROCESS

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Filed Jan. 24, 1957, Ser. No. 636,108
19 Claims. (Cl. 62—31)

The present invention relates to the refrigeration or liquefaction of gaseous material such as a gaseous fraction produced in a low temperature fractionating operation for separating gaseous mixtures.

In the separation of a mixture of component gases by low temperature fractionation employing heat exchange between the mixture to be fractionated and the cold products of the fractionation, conventional systems produce a liquid high boiling point fraction and a gaseous low boiling point fraction. Thus, in the case of air, liquid oxygen of high purity and gaseous nitrogen of high purity may be produced by such fractionation operations. Certain industries, because of the operations being conducted by them, desire to have not only a liquid high boiling point fraction of high purity but also require sizable quantities of a liquid low boiling point fraction. Thus, for example, in the case of separation of air into liquid oxygen as the high boiling point fraction and gaseous nitrogen as the low boiling point fraction, it would be desirable to provide a supply of liquid nitrogen. The Linde-Bronn process and modifications thereof require liquid nitrogen for refrigeration at temperatures below those obtainable with ammonia, utilize liquid nitrogen for scrubbing out the last traces of carbon monoxide from the final product and introduce liquid nitrogen into the product to bring about correct stoichiometric composition for the synthesis of ammonia. Also, liquid nitrogen is used in the laboratory for the liquefaction of hydrogen and helium in small quantities and as a cold reservoir for physical experiments at low temperatures.

Heretofore it has been necessary to employ external refrigeration means in order to liquefy the low boiling point fraction when this component was desired in liquid form. The utilization of external refrigeration is not only expensive from the standpoint of the initial cost of the installation of a refrigeration unit but also from the standpoint of power consumption and maintenance problems.

Accordingly, a principal object of the present invention is to provide an improved method and apparatus for liquefying a portion of the low boiling point fraction of a fractionating operation in which operation a gaseous mixture is normally fractionated to produce a gaseous low boiling point fraction and a liquid high boiling point fraction.

A further object of the present invention is to provide a method of liquefying a portion of the low boiling point fraction of a fractionating operation, in which method the refrigeration necessary for the liquefaction of the low boiling point fraction is provided by the operation itself without resort to external refrigeration means.

These and other important objects of the present invention will become more apparent from the following description of this invention taken in conjunction with the drawings in which similar reference characters denote similar elements throughout the several views:

FIGURE 1 is a diagrammatic representation of an air fractionating system illustrating the principles of the present invention;

FIGURE 2 is a diagrammatic representation of an air fractionating system which is a modification of that illustrated in FIGURE 1;

FIGURE 3 is a further diagrammatic representation of an air fractionating system illustrating a further modification of FIGURE 1; and



FIGURES 4 and 5 show further modifications which may be employed in the fractionating systems shown in FIGURES 1, 2 and 3.

In each of the fractionating systems illustrated in the accompanying drawings, the incoming mixture of gases to be separated into a liquid high boiling point fraction and a low boiling point fraction is compressed to a moderately high pressure and then refrigerated by heat exchange against a stream of the gaseous low boiling point fraction from the fractionating operation. After this heat exchange step, a sub-stream of the gaseous low boiling point fraction is compressed to a relatively high pressure and is then passed in heat exchange relation with a cold fluid from the fractionating operation. For the purpose of providing make-up refrigeration and the excess or additional refrigeration needed for liquefying the cooled compressed substream of the low boiling point fraction, a high pressure stream of the system, such as a minor portion of the partially cooled incoming gaseous mixture, is expanded while doing work. The excess refrigeration needed for liquefaction is supplied to the gaseous mixture and is then utilized for the liquefaction operation. Utilization of the excess refrigeration may be accomplished by heat exchanging the cooled compressed substream with the gaseous mixture to which the excess refrigeration has been supplied prior to the entry of the gaseous mixture into the high pressure stage of the rectification column or may be accomplished by passing the cooled compressed substream of low boiling point fraction in heat exchange with a fluid stream of the fractionating operation to which the excess refrigeration has been supplied. If desired, the stream of compressed low boiling point fraction may be serially passed in heat exchange relation with a stream of gaseous mixture on its way to the fractionating operation and a fluid stream of the fractionating operation, the excess refrigeration being supplied to the stream of gaseous mixture and to the fluid stream.

By the term "make-up refrigeration" as used in the specification and the claims is meant refrigeration to compensate for heat leaks into the system as well as that necessary to compensate for losses resulting from the difference in enthalpy between the incoming gaseous mixture and the outgoing products of rectification.

Although the incoming gaseous mixture has been cited as an example of a high pressure gaseous stream of which a portion may be expanded for producing make-up refrigeration as well as that necessary for liquefaction of the cooled compressed substream of low boiling point fraction, it will be apparent that other high pressure gaseous streams of the system will serve the purpose. Thus in the case of fractionating air to produce liquid nitrogen in accordance with the present invention, up to approximately 10% of the total high pressure gaseous nitrogen from the high pressure stage of the column may be employed.

Although the following specific description of the present invention is concerned with the separation of air into a liquid high boiling point fraction and a low boiling point fraction which is partially liquid and partially gaseous, it is to be understood that the principles of the present invention are not limited to the separation of air into these components but are equally applicable to any mixture of gases having relatively low and relatively high boiling point constituents.

Referring to FIGURE 1 of the drawings, compressed dry air substantially free of carbon dioxide and other impurities enters the system through a conduit **10**. A major portion of the incoming air passes through a path **12** of heat interchanger **14** and is carried by conduit **16** through expansion valve **18** to conduit **20** which introduces the cooled air stream at the required pressure

into the base of a high pressure stage 22 of the two-stage rectification column 24. The column is of conventional construction including a refluxing condenser 26 and a liquid collecting shelf 28 located below the condenser in the high pressure stage for collecting liquid high pressure nitrogen. The high and low pressure stages of the column are provided with suitable liquid-vapor contacting means, such as bubble trays. Conduit 30, including a pressure reducing valve 32, leads from the shelf 28 to the top portion of the other upper section or low pressure stage 34 of the column 24, and a conduit 36 conducts a stream of crude oxygen from the base of the high pressure stage 22 via pressure reducing valve 38 to an intermediate feed point of the low pressure stage 34. Conduit 40 leading from the top of the low pressure stage 34 conveys product nitrogen therefrom, and the oxygen product may be withdrawn from the low pressure stage in liquid or gaseous phase. In the illustrated cycle the oxygen product is withdrawn in liquid phase and is conducted by a conduit 42 to a liquid oxygen pump 44 and then through pass 46 of heat exchanger 14. The conduit 40 conducts the low pressure nitrogen product through pass 48 of the heat exchanger. The countercurrent flow relation of the product oxygen and nitrogen streams to the incoming air stream in exchanger 14 refrigerates the incoming air stream.

A portion of the total product nitrogen stream after passage through exchanger 14 is diverted at point 50 and is compressed to a relatively high pressure in pump or compressor 52. This diverted and compressed nitrogen stream is cooled by a cold fluid of the system, such as by countercurrent heat exchange against the oxygen and nitrogen product streams of the fractionating operation. For this purpose, a conduit 54 is connected between the pump 52 and pass 56 of exchanger 14. The cooled stream of compressed nitrogen from the cold end of the pass 56 is conducted by a conduit 58 to boiler coil 60 located in the pool of liquid crude oxygen collecting in the base of the high pressure stage 22. Refrigeration supplied to the compressed nitrogen stream when flowing through the coil 60 effects its liquefaction as described more fully below.

In order to provide make-up refrigeration for the system and to supply the refrigeration necessary to effect liquefaction of the compressed nitrogen stream, a minor portion of the total air stream is diverted at point 62 of pass 12 of exchanger 14 and is conducted to an expansion engine 64. The effluent of the expansion engine is approximately at the operating pressure of the high pressure section 22, and is merged with the main portion of the cooled air feed downstream of the expansion valve 18 at the point 66. Expansion of the diverted portion of the total air stream in the expansion engine 64 is such that the resulting increase in refrigeration provides a total refrigeration for the cycle in excess of the refrigeration normally required for proper operation of the rectification column 24. The excess refrigeration fed to the column in this manner provides the refrigeration required to effect liquefaction of the stream of compressed nitrogen flowing through the boiling coil 60. When the compressed nitrogen stream is at a pressure below the critical pressure of nitrogen, liquefaction of the compressed nitrogen stream may be accomplished in the boiling coil 60, whereas if the compressed nitrogen stream is at a pressure above the critical pressure of nitrogen actual liquefaction of the compressed nitrogen stream will not occur until the pressure of the stream is reduced to below the critical pressure of nitrogen. For example, if the pump 52 is designed to compress the nitrogen stream to 1000 p.s.i.g., and if the stream is passed through the boiling coil 60 at that pressure, its liquefaction will not occur until expanded to below the critical pressure of nitrogen, such as by means of an expansion valve 61 located downstream of the boiling coil 60. Whether the compressed nitrogen stream passes through the boiling coil at a pressure above or below the critical pressure of nitrogen, the refrigeration required to effect its liquefaction is added to the stream upon flowing through the boiling coil, and the required refrigeration comprises the excess refrigeration provided by operation of the expansion engine 64.



In the fractionating system shown in FIGURE 2 of the drawings, compressed and purified air enters the system through conduit 200. A major portion of the incoming air flows through passes 202 and 204 of exchangers 206 and 208, respectively, and is cooled by heat exchange with the returning cold products of the fractionating operation as described below. The cooled major portion of the air is then expanded in expansion valve 210 after the streams are recombined at point 212. The pressure of the air stream after expansion in valve 210 is substantially that required for column operation and the air stream is passed by conduit 214 and pass 216 of heat exchanger 220 to the lower section 22 of rectification column 24. The purpose of heat exchanger 220 will be described below.

Liquid oxygen surrounding condenser 26 in the upper or low pressure stage 34 of fractionating column 24 is fed to pump 222 and is delivered therefrom through conduit 224 to point 226 where the liquid oxygen stream branches to form two streams flowing in conduits 228 and 230. The proportion of liquid oxygen from conduit 224 flowing in each of conduits 228 and 230 is substantially the same as the proportion in which the entering air stream in conduit 200 is divided between passes 204 and 202, respectively, of heat exchangers 208 and 206. The liquid oxygen in conduits 228 and 230 flows through heat exchanger passes 232 and 234, respectively, of exchangers 208 and 206. The thusly warmed up streams of product oxygen may be merged as a single stream at point 236 and provide a supply of pure oxygen product.

High purity nitrogen is removed from the top of column 24 through conduit 238 and is passed in countercurrent heat exchange relation with the incoming air stream by flowing through pass 240 of heat exchanger 208. The stream is withdrawn from the heat exchanger through conduit 242 as high purity gaseous nitrogen product. A substream of high purity gaseous nitrogen is removed from the conduit 242 at point 244 and is compressed to a relatively high pressure in pump or compressor 246. The compressed substream of high purity nitrogen flows through conduit 248 and is divided at point 250 by conduits 252 and 254 to form two streams which are conducted through passes 256 and 258 of heat exchangers 206 and 208, respectively. The relative proportion of compressed high purity nitrogen in passes 256 and 258 are substantially the same as the relative proportion of the incoming air stream passing through the heat exchanger passes 202 and 204, respectively. The streams of cooled, compressed high purity nitrogen from heat exchanger passes 256 and 258 flow respectively through conduits 260 and 262 to point 264 where the streams merge and flow by way of conduit 266 through pass 268 of heat exchanger 220. The stream of cooled, compressed high purity nitrogen leaves the heat exchanger pass in heat exchanger 268 through conduit 270 which may include an expansion valve 271.

A stream of low purity nitrogen may be removed from the low pressure stage 34 of column 24 through conduit 272, the conduit 272 being joined to the column at a point intermediate the feed points of the expanded high pressure nitrogen and the expanded high pressure crude oxygen. The conduit 272 conducts the stream of low purity nitrogen to pass 274 of exchanger 206 in a direction countercurrent to the flow of the air stream. The resulting warmed-up stream of low purity nitrogen is withdrawn through conduit 276.

In order to provide make-up refrigeration for the system of FIGURE 2 and to supply refrigeration necessary to effect liquefaction of the substream of cooled, compressed nitrogen flowing through pass 268 of heat exchanger 220, a minor portion of the total air stream is

diverted from the heat exchanger passes **202** and **204** at points **278** and **280**, respectively, and is conducted through conduit **282** to an expansion engine **284** wherein the minor portion of the air stream is expanded with work to substantially the pressure required for the operation of column **24**. The effluent of the expansion engine is passed through conduit **286** and is merged at point **288** with the major air stream flowing in conduit **214**. By this arrangement a cold high pressure gaseous stream of the system is expanded while doing work and the refrigeration obtained is sufficient to provide the make-up refrigeration necessary for the system as well as the refrigeration necessary to effect liquefaction of the cooled, compressed high purity nitrogen stream. The refrigeration provided to effect liquefaction of the compressed high purity nitrogen stream is transferred to the nitrogen stream in the heat exchanger **220**. The high purity nitrogen stream will be liquefied in the heat exchanger **220** when compressed to below the critical pressure of nitrogen, and when compressed to above the critical pressure liquefaction will occur upon subsequent expansion to below the critical pressure, such as by expansion valve **271**.

Referring to FIGURE 3 of the drawings, compressed and purified air enters the system through a conduit **300** connected to branch conduits **302** and **304** which feed substreams to passes **310** and **312**, respectively, of the heat exchangers **306** and **308**. The cooled substreams of the major portion of the air stream are combined at the point **314** and then passed to an expansion valve **316**. The effluent of the expansion valve, at substantially the pressure required for operation of two stage column **24**, is fed by way of conduit **318** and pass **320** of heat exchanger **322** to the base of high pressure section **22** of column **24**.

Liquid oxygen is withdrawn from the column **24** and fed to a pump **324**. Liquid oxygen discharged from the pump is fed by way of conduit **326** to point **327** where it merges with conduits **328** and **329** connected to passes **330** and **332** of heat exchangers **306** and **308**, respectively. The liquid oxygen flowing through passes **330** and **332** in countercurrent heat exchange relation with the incoming air streams is warmed-up and may be subsequently merged into one stream at point **334** for delivery as high purity product oxygen.

Low purity nitrogen is removed from the low pressure section **34** of column **24** by way of conduit **336** and is conveyed to point **338** at which point it is divided into two streams of low purity nitrogen, flowing in conduits **340** and **342**. The low purity nitrogen in conduit **340** flows through pass **344** of heat exchanger **308** in countercurrent heat exchange relation with the incoming air stream and is removed from the heat exchanger through conduit **346**. The flow path of the low purity nitrogen in conduit **342** and its function will be described below.

High purity nitrogen is withdrawn from the top of column **24** through conduit **348** and passed through pass **350** of heat exchanger **306** in countercurrent heat exchange relation with the incoming air stream. The resulting stream of warmed-up high purity nitrogen is removed from exchanger **306** by conduit **352**. A substream of high purity gaseous nitrogen is withdrawn from the conduit **352** at point **354** and is compressed to a relatively high pressure in pump or compressor **356**. The resulting substream of compressed high purity nitrogen flows through heat exchange pass **358** of heat exchanger **360** where it is cooled in a manner described hereinafter. The cooled stream of compressed high pressure high purity nitrogen is conveyed by conduit **362** through pass **364** of heat exchanger **322**. For the purpose of cooling the compressed high purity nitrogen flowing through pass **358** and heat exchanger **360**, the substream of low purity nitrogen in conduit **342** is passed in countercurrent heat exchange relation through pass **366** of the heat exchanger **360**. The resulting warmed-up stream of low purity nitrogen flows from heat exchanger **306** through conduit **368** which may be joined with conduit **346** for the purpose of withdrawing the low purity nitrogen from the cycle.

In order to supply make-up refrigeration for the system and to provide the refrigeration required to effect liquefaction of compressed high purity nitrogen fed to the heat exchanger **322**, a minor portion of the partially cooled air stream is diverted from passes **310** and **312** of heat exchangers **306** and **308** at points **370** and **372**, respectively. The diverted streams are merged at the point **374** and passed through expansion engine or turbine **376** which expands the minor portion of the air stream to substantially the pressure required for the operation of column **24**. The effluent of the expansion engine passes through conduit **378** to point **380** where it merges with the main air stream flowing in conduit **318**. As is the case in FIGURES 1 and 2, the expansion of the minor portion of the total air stream increases the refrigeration to a level above that required for normal column operation and supplies the refrigeration necessary to effect liquefaction of the cooled compressed substream of high purity nitrogen.

The following will illustrate a specific example of the operation of the process of this invention. In the apparatus of FIGURE 3, 76,500 pounds of air per hour at a temperature of 50° F. and a pressure of 600 p.s.i.g. is introduced into the system through conduit **300**. The major portion of the air stream is divided between passes **310** and **312** of heat exchangers **306** and **308**, respectively, and flowed therethrough to expansion valve **316** where the cooled air stream is expanded to a pressure of 80 p.s.i.g. at a temperature of −275° F. A minor portion of the total incoming air stream, in this case approximately 27,000 pounds per hour, is removed from heat exchangers **306** and **308** at points **370** and **372** and expanded in expansion engine **376** to a pressure of approximately 80 p.s.i.g. at a temperature of −275° F. The expanded minor and major portions of the air stream are merged in conduit **318** and flow through heat exchanger **322** to the base of high pressure section **22** of column **24**. Expansion of the minor portion of the total air stream increases the total refrigeration available to an amount above that required for proper column operation. The excess refrigeration provides the refrigeration necessary to effect liquefaction of the compressed stream of high purity nitrogen stream flowing through pass **364** of the heat exchanger **322**.

High purity nitrogen at a rate of 2,350 pounds per hour at a pressure of 295 p.s.i.g. and a temperature of 100° F. flowing from compressor or pump **356** flows through pass **358** of exchanger **360** where it is cooled by a counter flowing stream of 1900 pounds per hour of impure nitrogen at a pressure of 7 p.s.i.g. and a temperature of −275° F. After this heat exchange, the cooled compressed substream of nitrogen is at a temperature of −195° F. and a pressure of 285 p.s.i.g. This stream passes via conduit **362** to heat exchanger pass **364** where it is liquefied and emerges as product liquid nitrogen at a pressure of 280 p.s.i.g. and a temperature of −270° F. As mentioned above, if the high purity nitrogen is compressed to a value above the critical pressure of nitrogen, liquefaction will not occur in the heat exchanger **322** but the refrigeration necessary to effect liquefaction will be added to the stream of high purity nitrogen. Subsequent expansion of the high purity nitrogen stream, downstream of the heat exchanger **322**, will result in liquefaction of the high purity nitrogen.

When employing the usual pressures associated with normal operation of a two-stage fractionating column, up to about 7% of the total nitrogen fed to the system may be liquefied in accordance with the process of the present invention. If air under sufficiently high pressure is available, up to about 20% of the total nitrogen may be liquefied. The limitation on the upper amount of total nitrogen that may be liquefied is determined by the quantity of partially cooled compressed air that may be passed through the particular expansion engine used. This in turn is determined by the main heat exchanger demands for optimum operation. The amount of refrigeration which is determined by the foregoing factors and

supplied to the cycle as excess refrigeration determines the percentage of nitrogen that may be liquefied.

In FIG. 4, an arrangement is shown for transferring to a stream of compressed nitrogen the necessary refrigeration to effect its liquefaction by passing the stream of compressed nitrogen in heat exchange with a relatively cold fluid stream of the fractionating system which carries the excess refrigeration. As shown, a stream of air feed is introduced into the high pressure section **22** by way of a conduit **20**, the air feed including the excess refrigeration. The crude oxygen collecting in a pool **21** in the base of the high pressure section thus also includes the excess refrigeration. A stream of compressed nitrogen flows through a pass **23** of a heat exchanger **25** supplied with a source of liquid crude oxygen by way of a conduit **27**, a conduit **29** is connected from the heat exchanger **25** to return crude oxygen vapors to the column. Other cold fluids of the system may be employed, such as liquefied high pressure nitrogen, for example. In FIGURE 5, an arrangement is shown for refrigerating a stream of compressed nitrogen to the degree necessary to effect its liquefaction by heat exchange with two relatively cold fluid streams of the fractionating system. The stream of compressed nitrogen is first passed through a pass **31** of a heat exchanger **33** included in the air feed conduit **20**, and then through the pass **23** of heat exchanger **25** in a manner similar to the arrangement of FIGURE 4. The feature of adding the necessary refrigeration to the compressed nitrogen stream to effect its liquefaction by heat exchange with the stream of air feed and with liquid crude oxygen makes it possible to more easily obtain uniform column operation. Although the foregoing invention has been described in connection with a two stage fractionating column, its operation is applicable to a single stage column. However, since the purity of the nitrogen product of a single stage fractionating column is low when high purity oxygen is desired, the liquid nitrogen would not be satisfactory for many purposes for which relatively pure liquid nitrogen is required, for example, the Linde-Bronn process. In the case of the liquefaction of a low boiling fraction of a gaseous mixture other than air, such as a mixture of gaseous hydrocarbons, the use of one or more single stage columns is particularly applicable.

The foregoing desciption of the present invention is for the purpose of illustration only and is not limiting to the scope of the same which is set forth in the appended claims.

This is a continuation-in-part of copending application Serial No. 388,745, filed October 28, 1953, for Method and Apparatus for Liquefying a Gas, now abandoned.

I claim:

1. Method of refrigerating gaseous material under superatmospheric pressure in a fractionating operation, in which operation compressed gaseous feed mixture is cooled and separated in a fractionating zone producing cold fractions of the gaseous mixture at least one of which is passed in heat exchange relation with the feed mixture to cool the feed mixture and in which make-up refrigeration is provided for the fractionating operation,

comprising the steps of establishing heat interchange between gaseous material under superatmospheric pressure and at least one relatively cold fluid of the fractionating operation to transfer a quantity of refrigeration to the gaseous material under superatmospheric pressure,

the quantity of refrigeration transferred to the gaseous material under superatmospheric pressure providing a total refrigeration content of the gaseous material sufficient to effect liquefaction of the gaseous material when under a pressure no greater than the critical pressure of the gaseous material.

withdrawing the gaseous material containing transferred refrigeration from the fractionating operation after the heat interchange,

and expanding a high pressure fluid of the fractionating operation while doing work to provide refrigeration in excess of the make-up refrigeration for the fractionating operation,

the refrigeration in excess of the make-up refrigeration compensating for the quantity of refrigeration transferred to the gaseous material withdrawn from the fractionating operation.

2. Method of refrigerating gaseous material as defined in claim 1 in which said one relatively cold fluid of the fractionating operation in heat interchange with the gaseous material under superatmospheric pressure comprises cooled feed mixture.

3. Method of refrigerating gaseous material as defined in claim 1 in which said one relatively cold fluid of the fractionating operation in heat interchange with the gaseous mixture under superatmospheric pressure comprises a fluid formed in the fractionating zone.

4. Method of refrigerating a fraction of a gaseous mixture separated in a fractionating operation, in which operation compressed gaseous feed mixture is cooled and separated in a fractionating zone producing different boiling point fractions of the gaseous mixture and in which make-up refrigeration is provided for the fractionating operation,

comprising the steps of withdrawing one fraction from the fractionating zone,

passing withdrawn fraction in heat exchange relation with a relatively warm fluid of the fractionating operation to warm the withdrawn fraction,

compressing warm withdrawn fraction to a relatively high pressure,

establishing heat interchange between compressed fraction and at least one relatively cold fluid of the fractionating operation to transfer a quantity of refrigeration to the compressed fraction,

the quantity of refrigeration transferred to the compressed fraction providing a total refrigeration content of the compressed fraction sufficient to effect liquefaction of the compressed fraction when under a pressure no greater than the critical pressure of the compressed fraction,

withdrawing the compressed fraction containing transferred refrigeration from the fractionating operation after the heat interchange,

and expanding a high pressure fluid of the fractionating operation to provide refrigeration in excess of the make-up refrigeration for the fractionating operation,

the refrigeration in excess of the make-up refrigeration compensating for the quantity of refrigeration transferred to the compressed fraction withdrawn from the fractionating operation.

5. Method of refrigerating a fraction of a gaseous mixture as defined in claim 4 in which said one relatively cold fluid of the fractionating operation in heat interchange with the compressed fraction comprises cooled feed mixture.

6. Method of refrigerating a fraction of a gaseous mixture as defined in claim 4 in which said one relatively cold fluid of the fractionating operation in heat interchange with the compressed fraction comprises a relatively cold fluid formed in the fractionating zone.

7. Method of refrigerating low boiling point fraction produced in a fractionating operation, in which operation gaseous mixture is separated in a fractionating zone producing low boiling point fraction and in which make-up refrigeration is provided,

comprising the steps of withdrawing low boiling point fraction from the fractionating zone,

passing withdrawn low boiling point fraction in heat interchange with relatively warm fluid to warm low boiling point fraction,

compressing warm low boiling point fraction to a higher pressure,

adding a quantity of refrigeration from the fractionat-

ing operation to compressed low boiling point fraction sufficient to effect liquefaction of compressed low boiling point fraction when under a pressure no greater than the critical pressure of the low boiling point fraction,

and expanding a high pressure fluid of the fractionating operation to provide a quantity of refrigeration for the fractionating operation to compensate for the refrigeration added to the compressed low boiling point fraction.

8. The method of refrigerating low boiling point fraction produced in a fractionating operation, in which operation gaseous feed mixture is fractionated in a fractionating zone producing cold products including gaseous low boiling point fraction,

comprising the steps of withdrawing a stream of gaseous low boiling point fraction from the fractionating zone,

passing withdrawn gaseous low boiling point fraction in heat exchange relation with relatively warm fluid to warm the gaseous low boiling point fraction,

compressing a stream of warm gaseous low boiling point fraction to a relatively high pressure,

passing compressed low boiling point fraction in heat interchange with relatively cold fluid of the fractionating operation to transfer refrigeration to the compressed low boiling point fraction and provide a total refrigeration content of the low boiling point fraction sufficient to effect liquefaction of the low boiling point fraction when under a pressure no greater than the critical pressure of the low boiling point fraction,

withdrawing refrigerated low boiling point fraction from the fractionating operation,

and expanding a high pressure fluid of the operation to provide refrigeration to compensate for refrigeration removed from the fractionating operation with the withdrawn refrigerated low boiling point fraction.

9. Method of refrigerating low boiling point fraction produced in a fractionating operation, in which operation gaseous mixture is separated in a fractionating zone producing cold low boiling point fraction and in which make-up refrigeration is provided for the operation,

comprising the steps of withdrawing low boiling point fraction from the fractionating zone,

passing withdrawn low boiling point fraction in heat interchange with a relatively warm fluid of the fractionating operation to warm low boiling point fraction,

compressing warm low boiling point fraction to a higher pressure,

passing compressed low boiling point fraction in heat interchange with relatively cold fluid of the fractionating operation to cool compressed low boiling point fraction,

expanding high pressure fluid of the fractionating operation while doing work to provide refrigeration in excess of the make-up refrigeration,

and transferring excess refrigeration to cool compressed low boiling point fraction,

the excess refrigeration transferred to cool compressed low boiling point fraction providing a total refrigeration content of compressed low boiling point fraction sufficient to effect liquefaction of the low boiling point fraction when under a pressure no greater than the critical pressure of the low boiling point fraction.

10. Method of refrigerating low boiling point fraction produced in a fractionating operation, in which operation gaseous feed mixture is separated in a fractionating zone producing cold products including gaseous low boiling point fraction,

comprising the steps of withdrawing a stream of gaseous low boiling point fraction from the fractionating zone,



passing withdrawn gaseous low boiling point fraction in heat exchange relation with relatively warm fluid to warm the gaseous low boiling point fraction,

compressing a stream of warm gaseous low boiling point fraction to a relatively high pressure,

passing compressed low boiling point fraction in heat exchange with relatively cold fluid of the fractionating operation to cool compressed low boiling point fraction,

passing cool compressed low boiling point fraction in heat interchange with relatively cold fluid of the fractionating operation to transfer a quantity of refrigeration to the cool compressed low boiling point fraction sufficient to effect liquefaction of the low boiling point fraction when under a pressure no greater than the critical pressure of the low boiling point fraction,

withdrawing refrigerated low boiling point fraction from the fractionating operation,

and expanding a high pressure fluid of the fractionating operation to provide a quantity of refrigeration for the fractionating operation in excess of the make-up refrigeration and at least equal to the quantity of refrigeration transferred to the compressed low boiling point fraction withdrawn from the fractionating operation.

11. Method of refrigerating low boiling point fraction as defined in claim 10 in which relatively cold fluid of the fractionating operation in heat interchange with cool compressed low boiling point fraction comprises relatively cold gaseous mixture.

12. Method of refrigerating low boiling point fraction as defined in claim 10 in which relatively cold fluid of the fractionating operation in heat interchange with cool compressed low boiling point fraction comprises a relatively cold fluid formed in the fractionating zone.

13. Method of refrigerating low boiling point fraction as defined in claim 10 in which relatively cold fluid of the fractionating operation in heat interchange with cool compressed low boiling point fraction comprises relatively cold feed mixture and relatively cold liquid formed in the fractionating zone and in which the cool compressed low boiling point fraction is passed in heat interchange with the cold feed mixture and then in heat interchange with the cold liquid formed in the fractionating zone.

14. Method of refrigerating nitrogen produced in an air fractionating operation, in which operation air feed is cooled and separated in a fractionating zone producing cold products including cold gaseous nitrogen,

comprising the steps of withdrawing a stream of cold gaseous nitrogen from the fractionating zone,

passing withdrawn gaseous nitrogen in heat exchange relation wtih relatively warm fluid of the fractionating operation to warm the gaseous nitrogen,

compressing a stream of warm gaseous nitrogen to a relatively high pressure,

passing compressed nitrogen in heat exchange with a relatively cold fluid of the fractionating operation to cool compressed nitrogen,

passing cool compressed nitrogen in heat interchange with relatively cold fluid of the fractionating operation to transfer a quantity of refrigeration to the cool compressed nitrogen sufficient to effect liquefaction of the nitrogen when under a pressure no greater than the critical pressure of the low boiling point fraction,

withdrawing refrigerated nitrogen from the fractionating operation,

and expanding a high pressure fluid of the fractionating operation with the production of work to provide a quantity of refrigeration for the fractionating operation in excess of the make-up refrigeration required for the fractionating operation and at least equal to the quantity of refrigeration transferred to the compressed nitrogen withdrawn from the fractionating operation.

15. Method of refrigerating nitrogen as defined in claim 14 in which the relatively cold fluid of the fractionating operation passed in heat interchange with cool compressed nitrogen comprises cooled air feed.

16. Method of refrigerating nitrogen as defined in claim 14 in which the relatively cold fluid of the fractionating operation passed in heat interchange with cool compressed nitrogen comprises a fluid formed in the fractionating zone.

17. Method of refrigerating nitrogen as defined in claim 14 in which relatively cold fluid of the fractionating operation in heat interchange with cool compressed nitrogen comprises cooled air feed and a cold liquid formed in the fractionating zone and in which the cool compressed nitrogen is passed in heat interchange with the cooled air feed and then in heat interchange with the cold liquid formed in the fractionating zone.

18. Method of refrigerating nitrogen as defined in claim 17 in which high purity nitrogen fraction is separated from the air feed in the fractionating zone,

in which the compressed nitrogen comprises high purity nitrogen withdrawn from the fractionating zone,

and in which the compressed nitrogen is cooled upon heat interchange with relatively cold high purity nitrogen under lower pressure.

19. Apparatus for refrigerating low boiling point fraction produced in a fractionating system including fractionating means for separating cool gaseous mixture into cold fractions of the gaseous mixture including a relatively low boiling point fraction and a heat exchange system for cooling the gaseous mixture by heat interchange with at least one relatively cold fraction of the gaseous mixture.

comprising conduit means for withdrawing cool low boiling point fraction from the fractionating means,

first heat exchange means for passing withdrawn low boiling point fraction in heat interchange with a relatively warm fluid to warm the low boiling point fraction,

compressor means for compressing the warm low boiling point fraction to a relatively high pressure,



conduit means for passing compressed low boiling point fraction in heat interchange with a relatively cold fluid of the fractionating system to cool the compressed low boiling point fraction,

second heat exchange means for establishing heat interchange between cool compressed low boiling point fraction and a relatively cold fluid of the fractionating system to transfer a quantity of refrigeration to the cool compressed low boiling point fraction sufficient to effect liquefaction of the low boiling point fraction when under a pressure on greater than the critical pressure of the low boiling point fraction,

conduit means communicating with the second heat exchange means for withdrawing refrigerated low boiling point fraction from the fractionating system,

and expansion engine means for expanding with work a high pressure fluid of the fractionating system,

the expansion engine means having a capacity to provide a quantity of refrigeration in excess of the make-up refrigeration required for the fractionating system and at least equal to the quantity of refrigeration transferred to the compressed low boiling point fraction withdrawn from the fractionating system.

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