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NITROGEN LIQUEFACTION WITH PLURAL WORK EXPANSION OF FEED AS REFRIGERANT
Filed Oct. 8, 1965 6 Sheets-Sheet 1

FIG. 1

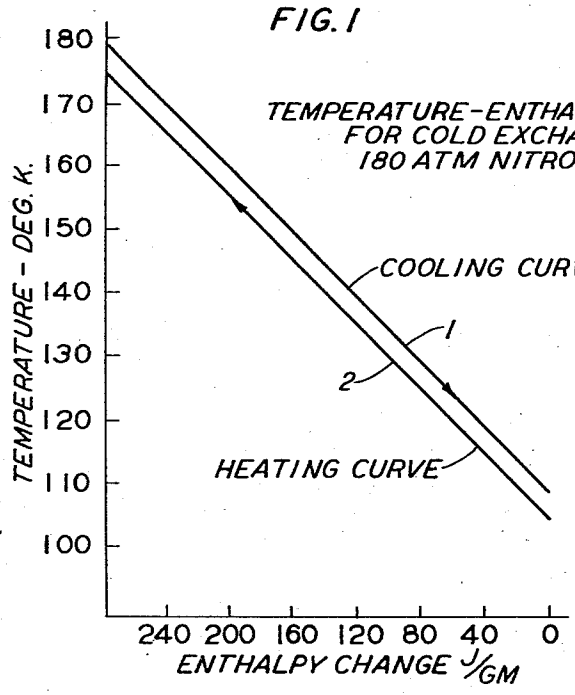
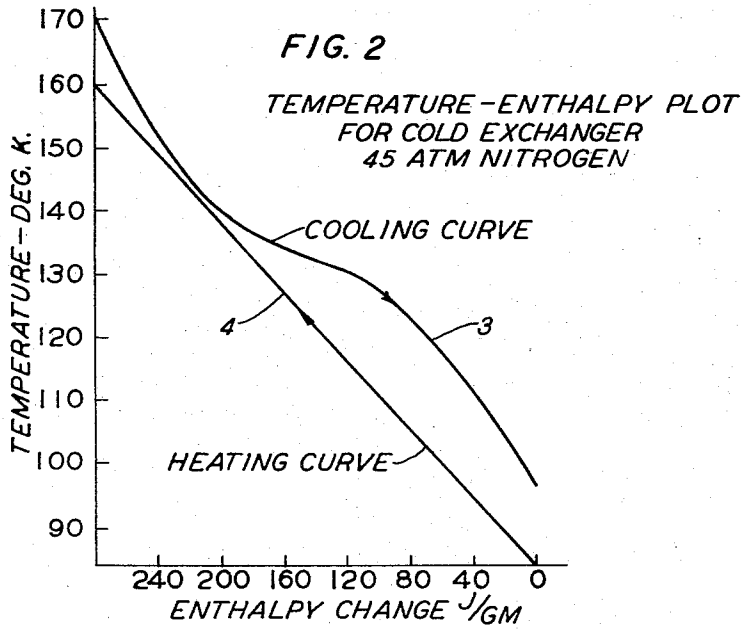



FIG. 2

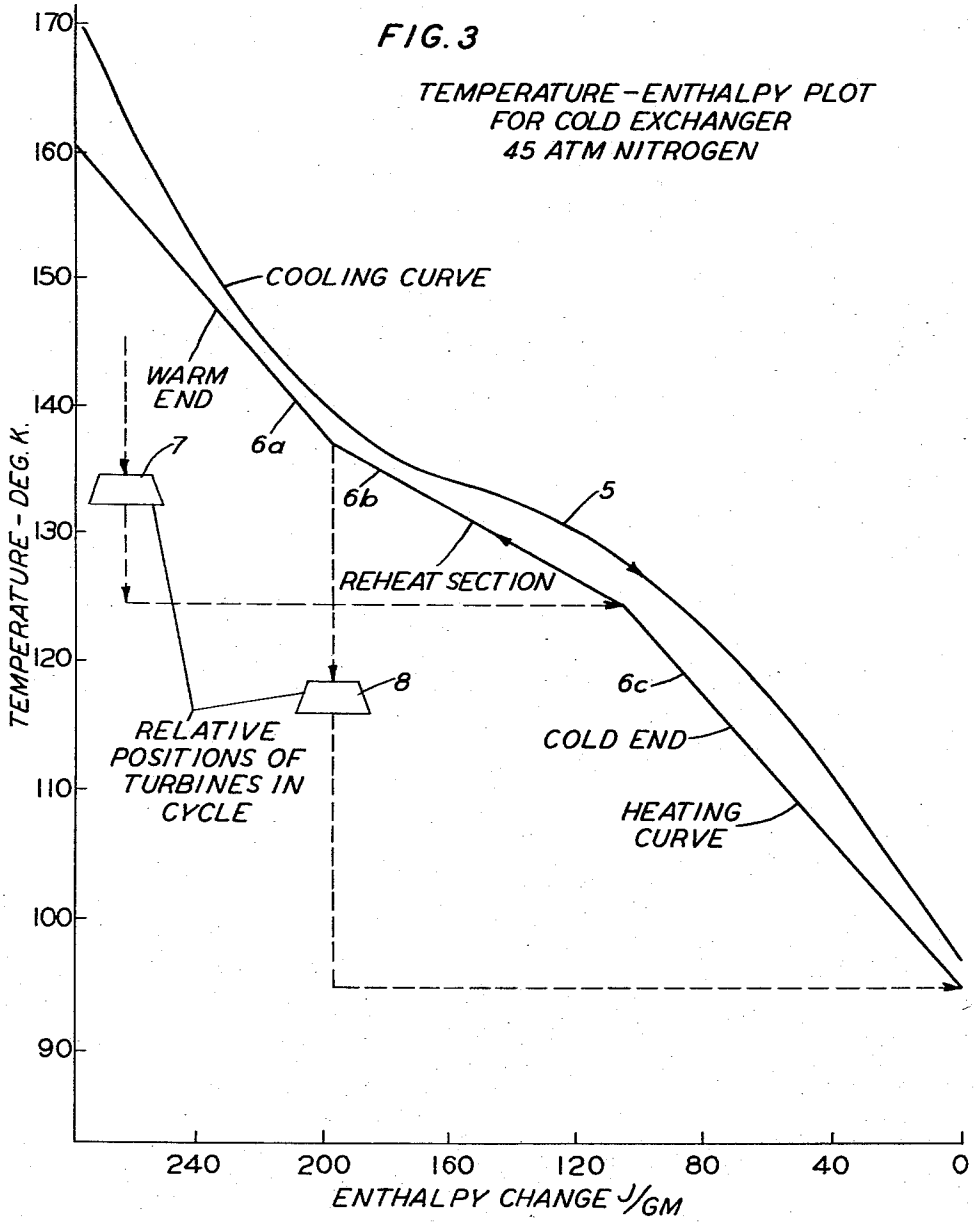



INVENTORS DONALD L. SMITH
JOHN L. FERRELL
BY
Jonathan Blount
ATTORNEY

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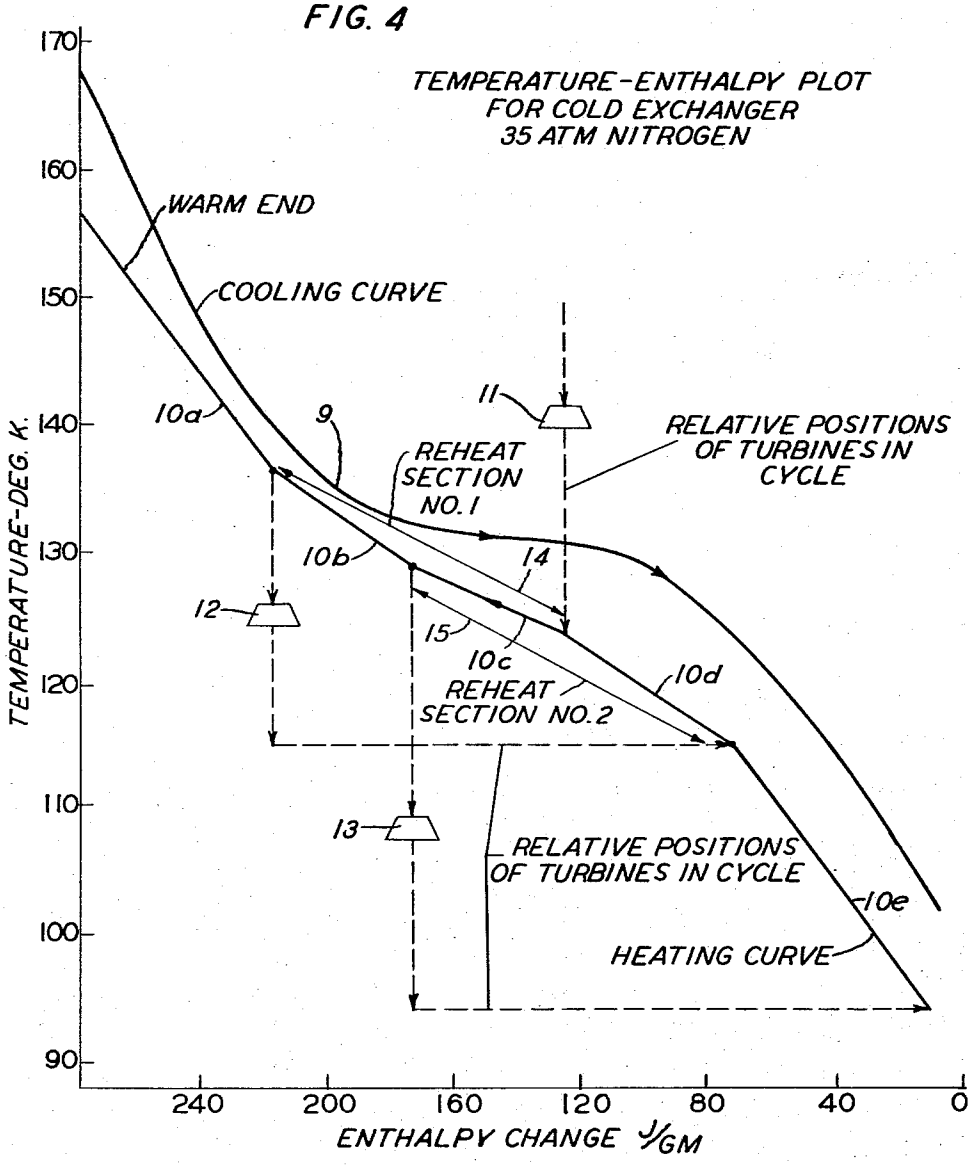
FIG. 3

TEMPERATURE-ENTHALPY PLOT FOR COLD EXCHANGER 45 ATM NITROGEN




INVENTORS DONALD L. SMITH
BY JOHN L. FERRELL
Jonathan Plant
ATTORNEY

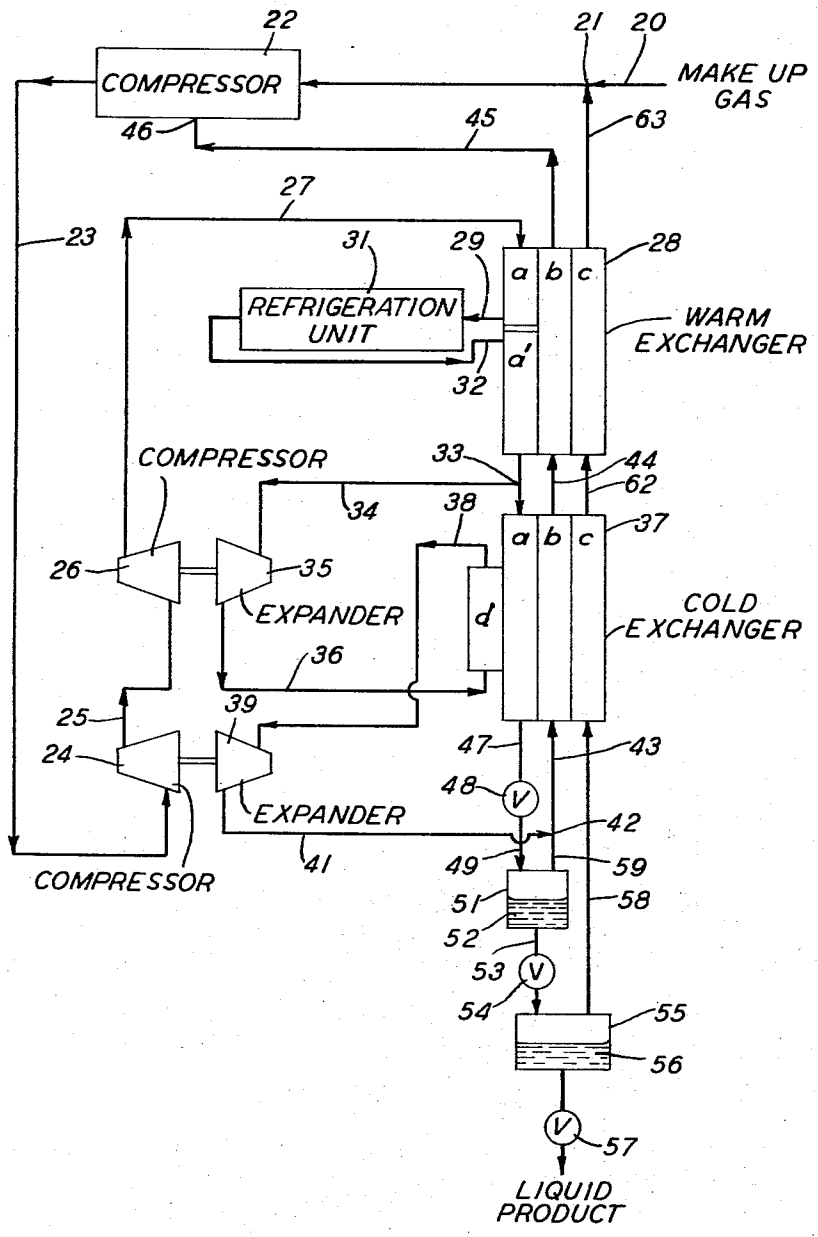
FIG. 4




INVENTORS DONALD L. SMITH
JOHN L. FERRELL
BY
Jonathan Blount
ATTORNEY

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FIG. 5
NITROGEN REFRIGERATION CYCLE WITH DOUBLE EXPANSION & REHEAT




INVENTORS DONALD L. SMITH
JOHN L. FERRELL
BY
Jonathan Blount
ATTORNEY

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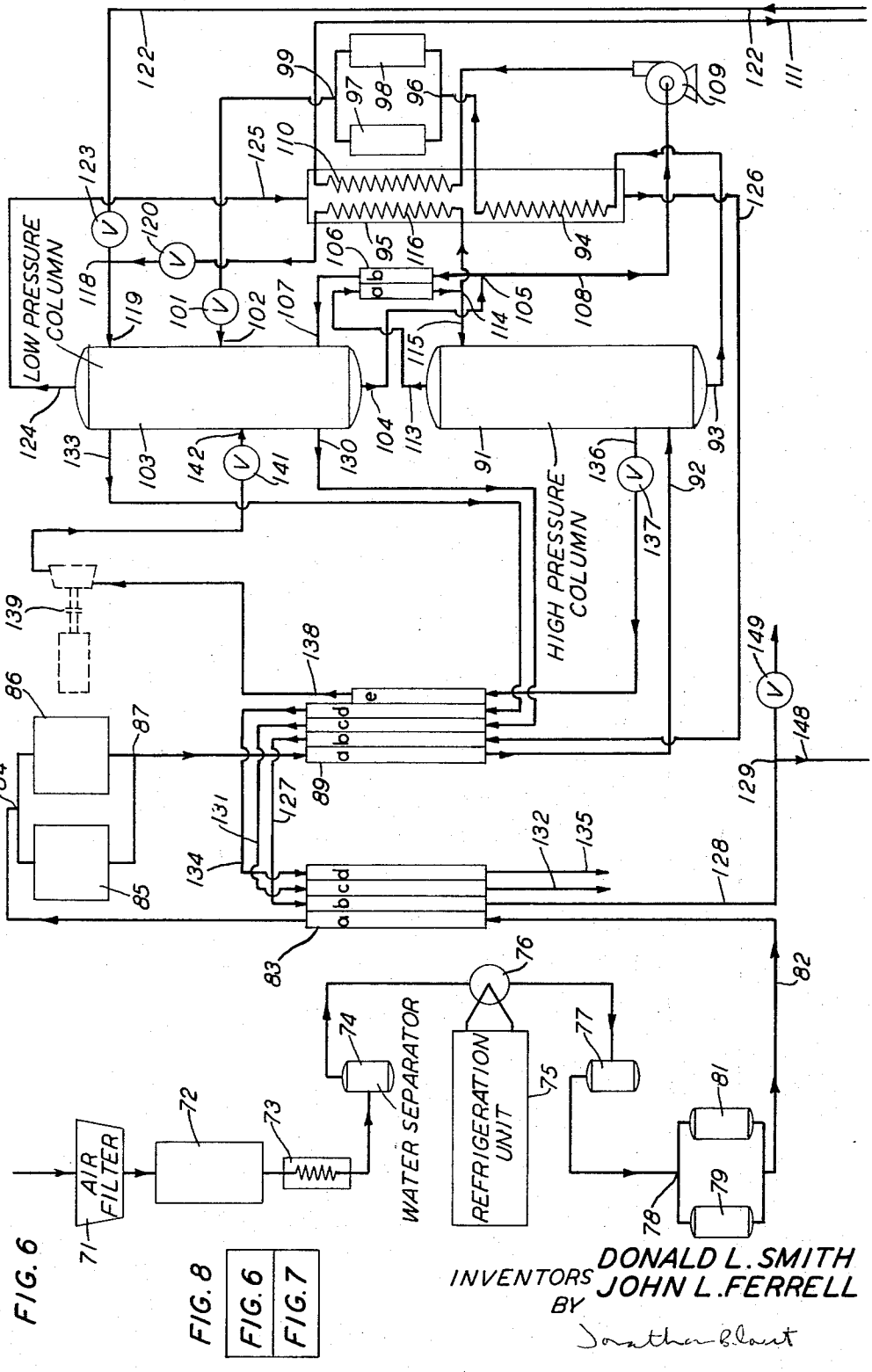



FIG. 6

FIG. 8

| FIG. 6 | FIG. 7 |
|---|---|

INVENTORS DONALD L. SMITH
JOHN L. FERRELL
BY Jonathan Blount
ATTORNEY

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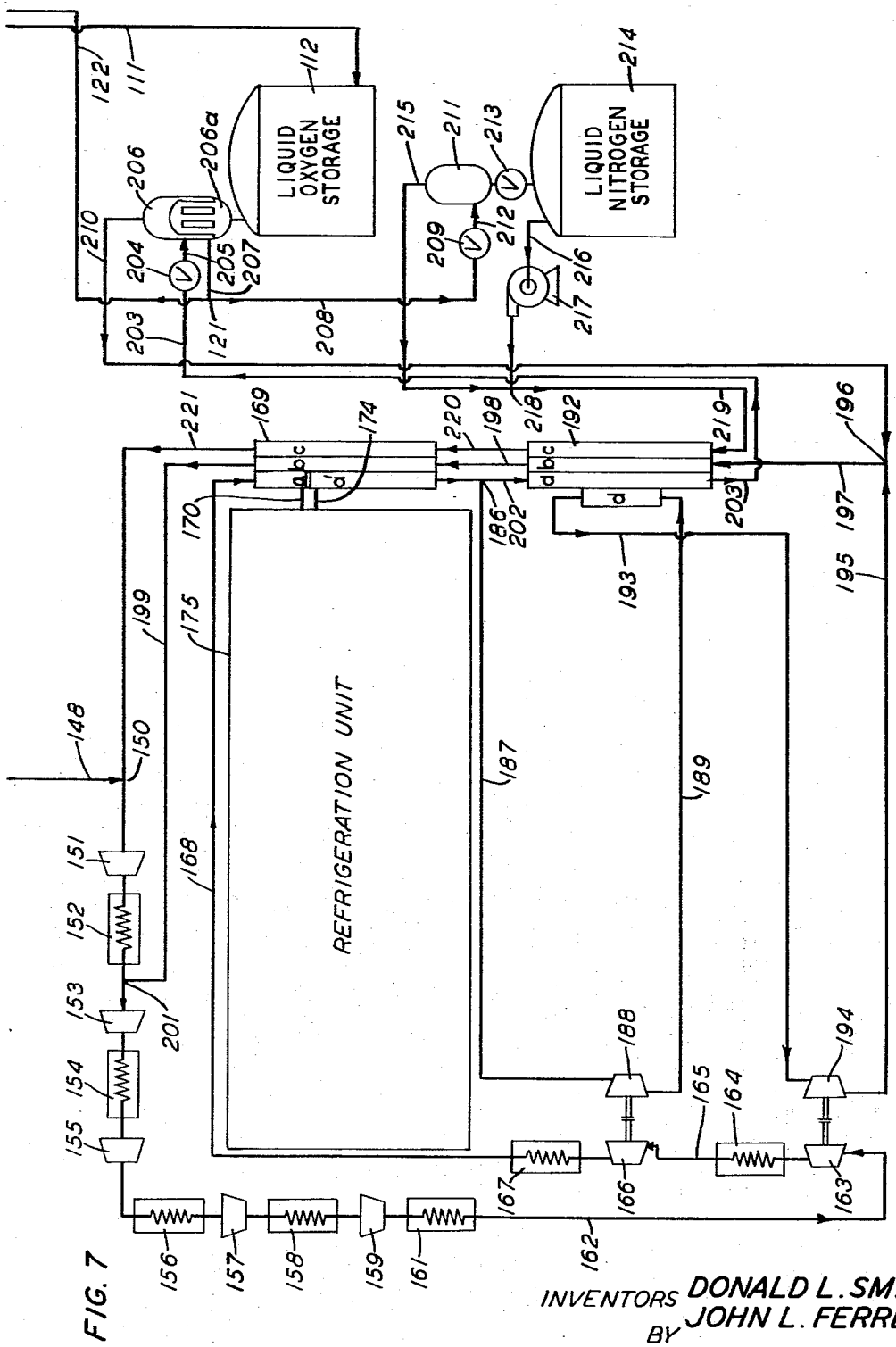



FIG. 7

INVENTORS DONALD L. SMITH
JOHN L. FERRELL

BY Jonathan Blount

ATTORNEY

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3,358,460

# NITROGEN LIQUEFACTION WITH PLURAL WORK EXPANSION OF FEED AS REFRIGERANT

Donald L. Smith, Berkeley Heights, and John L. Ferrell, North Plainfield, N.J., assignors to Air Reduction Company, Incorporated, New York, N.Y., a corporation of New York

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11 Claims. (Cl. 62—9)

This invention relates in general to the separation and liquefaction of low-boiling gases; and more particularly, to the liquefaction of nitrogen.

It is advantageous to operate liquefaction systems for low-boiling gases at relatively low head-pressures, say, of the order of 600 to 1,100 pounds per square inch absolute, since under such conditions an improved product may be realized while effecting substantial reductions in capital and maintenance expenditures. For example, centrifugal compression and expansion machinery, which is adapted for use in a relatively low pressure range, operates in such a manner that the product is substantially free of oil contamination. In addition, less expensive types of heat exchangers can be employed in the lower pressure ranges.

However, many liquefaction systems employing head-pressures within the range mentioned have the disadvantage of being thermodynamically inefficient. A possible explanation for this is that in a system employing a relatively high head-pressure, the high pressure stream in the cold-leg heat exchanger cools substantially as a straight-line function of temperature, whereas this is not true in a system employing a relatively low head-pressure. In the latter, the high-pressure stream undergoes a change in the cooling rate within the low temperature range which causes an inflection in the cooling curve, thereby producing a substantial temperature spread with the warming curve of the low temperature returning stream. This discrepancy leads to the consumption of substantial amounts of power, making such a system inefficient.

Accordingly, it is a principal object of this invention to improve the efficiency of liquefaction systems for low-boiling gases; and more particularly, to provide a liquefaction cycle for low-boiling gases under substantially reduced head-pressures which is characterized by greater thermodynamic efficiency than heretofore achieved in the low-pressure range. An ancillary object of the invention is to provide a cycle for the liquefaction of low-boiling gases, more particularly nitrogen, which operates at increased efficiency to produce a purer product, coupled with decreased maintenance and capital costs compared to similar prior art cycles.

These and other objects are realized in accordance with the present invention in a cycle for the liquefaction of low-boiling gases, more particularly, nitrogen, which contemplates the use of head-pressures within the range 600 to 1,100 pounds per square inch absolute, wherein a major portion of the pressurized stream is deployed to cool a minor portion thereof, without any substantial liquefaction occurring during this heat exchange. The salient feature of this arrangement is the work-expansion of the deployed major portion in two or more steps with one or more reheat steps intervening.

At head-pressures within the range, say, 600 to 1,100 pounds per square inch absolute, an arrangement of the type mentioned performs the function of approximating the shape of the low-pressure warming characteristic of the returning streams in the cold-leg heat exchanger to the inflected shape of the cooling characteristic of the high-pressure stream, thereby decreasing the temperature



spread between the characteristics and increasing the thermodynamic efficiency of the system.

For the purposes of illustration, the invention is described with reference to a system for air separation and the liquefaction of oxygen and nitrogen, in which the stream of nitrogen gas from the separator is first compressed through seven stages, then partially cooled, after which the initial stream is separated into two streams. The first stream, about two-thirds by volume, is work-expanded, then reheated, and again work-expanded. This expanded component combines with returning cold vapor, and then passes back through heat exchangers countercurrent to the second stream which consists of the remaining third of the initial stream. The second stream is cooled in the heat exchangers without liquefaction after which it passes through a throttle-valve for isenthalpic expansion, whereby a portion is converted to liquid which is separated out from the gaseous phase in a vapor-liquid separator. This liquid is again isenthalpically expanded to a pressure slightly above atmospheric pressure, at which pressure the liquid fraction is again separated out and stored. The low pressure vapor, including flash vapor from the surface of the stored liquid, is returned through the heat exchangers in countercurrent with the high pressure streams from which heat is absorbed, to the first compression stage for recycling through the system.

Whereas in the particular embodiment disclosed, the nitrogen liquefaction system includes two work-expansion steps separated by a reheat step, it will be apparent to those skilled in the art that improved results might be obtained under certain circumstances by the inclusion of additional work expansion and reheat steps.

By way of further illustrating the present invention, a nitrogen liquefaction system is disclosed in combination with an air separation system, in such a manner that a portion of the liquid nitrogen product serves as a refrigerating reflux for one of the rectification columns of the air separation system, and also, as a refrigerant for condensing flash vapor rising from the surface of the stored liquid oxygen.

Although the present invention is described herein with reference to a nitrogen liquefaction system, it will be understood by those skilled in the art that the principles disclosed are applicable to the liquefaction of any gas having a boiling point below about —112° F., including, for example, oxygen, ethane, ethylene, methane, argon, fluorine, carbon monoxide, neon, hydrogen and helium.

Other objects, features, and advantages of the system will be apparent from a detailed study of the specification hereinafter with reference to the attached drawings, in which:

FIGURES 1, 2, 3, and 4 are graphs illustrating the theory of the present invention, showing temperature in degrees Kelvin plotted against enthalpy change for the cooling and heating curves in the cold-leg exchanger of a nitrogen liquefaction system. FIGURE 1 illustrates the characteristics of a prior art system having a head-pressure of 180 atmospheres; FIGURE 2 illustrates characteristics of a prior art system utilizing a reduced head-pressure of 45 atmospheres; FIGURE 3 illustrates characteristics of an improved system in accordance with the present invention at 45 atmospheres head-pressure employing two work expansion steps; and FIGURE 4 shows the characteristics of a projected system at 35 atmospheres head-pressure employing three work expansion steps in accordance with the present invention;

FIGURE 5 shows a nitrogen liquefaction cycle in accordance with the present invention, in a block diagram schematic; and

FIGURES 6 and 7 show an over-all detailed schematic for a combined air separation and oxygen and nitro-

gen liquefaction system in accordance with the present invention, the two figures adapted to be fitted together in the manner indicated in FIGURE 8.

An objective of this liquefaction cycle is to minimize the power consumption requirements. In order to achieve low power consumption, the temperature difference between the countercurrent streams in the heat exchangers should be kept to a minimum.

In FIGURE 1 of the drawings, which shows temperature in degrees Kelvin plotted against change in enthalpy, in joules per gram-mol, for the cold exchanger in a nitrogen liquefaction system subject to 180 atmospheres head-pressure, the cooling curve **1** for the high pressure stream and the warming curve **2** for the low pressure return stream are both relatively straight line characteristics of approximately the same slope. Because of this fact, the temperature difference $\Delta T$ between the cooling and warming streams remains substantially uniform throughout the exchanger, thus making a multi-step work expansion with intervening reheat of no particular advantage in such a system.

Let us refer, now, to FIGURE 2 of the drawings. This shows a plot of the same parameters for the cold exchanger in a nitrogen liquefaction system subject to a head pressure of 45 atmospheres. It is apparent that at the lower head-pressure the cooling curve **3** of the high pressure stream is substantially inflected, producing a substantial spread, or temperature difference $\Delta T$, with the warming curve **4** at the lower end of the scale. As explained before, this spread in $\Delta T$ makes the system thermodynamically inefficient, inasmuch as additional power must be consumed to make up this difference.

In order to remedy this defect, and to provide a system which is more thermodynamically efficient at the lower head-pressures, the present invention contemplates that the shape of the warming characteristic in the cold-leg heat exchanger should be approximated to the inflected shape of the cooling curve. This is brought about by causing components of the warming stream to undergo a plurality of work expansion steps with intervening reheating.

For example, FIGURE 3 of the drawings shows curves plotted for a nitrogen liquefaction system similar to that represented in FIGURE 2, subject to 45 atmospheres head-pressure, but modified to include an auxiliary stream which undergoes two work expansion steps, in the positions indicated by **7** and **8**, and an intervening reheat step in the cold-leg heat exchanger running countercurrent with the cooling stream. In this plot, the cooling curve **5** is inflected, and is similar to cooling curve **3** of FIGURE 2. The warming curve in this modified system comprises sections **6***a*, **6***b*, and **6***c*, whose slopes tend to conform at the different levels to the slope of the cooling curve **5**, thereby increasing the thermodynamic efficiency of the system.

FIGURE 4 of the drawings shows a nitrogen liquefaction system subject to a still lower head-pressure, 35 atmospheres, in which the same parameters are plotted, as in the foregoing figures. The cooling curve **9** at this low head-pressure sustains an even greater inflection. In order to compensate for this in accordance with the present invention, three work expansion steps and two reheat sections are included as indicated schematically by the expanders **11**, **12**, and **13**, and arrows **14** and **15**. This produces an inflected warming curve **10***a*, **10***b*, **10***c*, **10***d*, and **10***e* which approximates the shape of cooling curve **9**.

It will be understood that this approach can be applied to the use of even a larger number of work expansion steps and intervening reheat steps.

A nitrogen liquefaction system embodying the principles set forth in the foregoing paragraphs is shown in block diagram in FIGURE 5 of the drawings.

A stream of make-up gas, comprising nitrogen, say, 99.99% pure, at substantially atmospheric pressure and



temperature, is brought into the system through conduit **20**, which flows into junction **21**. This stream is compressed through a plurality of compression stages **22** to a pressure of, say, 435 pounds per square inch absolute. The stream then passes out through conduit **23** to a pair of centrifugal compression stages **24** and **26**, connected by conduit **25**, where it is further compressed to a pressure of 670 pounds per square inch absolute, passing out through conduit **27**.

The highly compressed stream then passes into channel *a* of warm-leg heat exchanger **28** where it is cooled to about −40° F. It is then withdrawn from an intermediate point in the heat exchanger through conduit **29**, and passed through a refrigerator **31**, where it is cooled, say, to −101° F., before passing back into channel *a'* of heat exchanger **28** through conduit **32**.

The high pressure primary stream, cooled to about −130° F., passes out of heat exchanger **28** to junction **33**, where it is separated into two streams. The first, or major stream, comprising about two-thirds by volume, passes through conduit **34** to a work expansion stage **35**, where it is expanded to a pressure of about 150 pounds per square inch absolute, at a temperature of −236° F. The cooled, expanded major stream then passes out through conduit **36** and into channel *d* of cold-leg heat exchanger **37**, where it is reheated to, say, −213° F. It then passes out through conduit **38** to a second work expansion stage **39**, where it is expanded to a pressure of, say, 40 pounds per square inch absolute, and a temperature of −289° F.

This cooled, expanded medium-low pressure stream then flows into junction **42**, where, joined by a medium low pressure stream from conduit **59**, it flows through conduit **43** into channel *b* of heat exchanger **37**, and through conduit **44** into channel *b* of heat exchanger **28**, where it absorbs heat from counterflowing high pressure cooling streams. It then leaves heat exchanger **28** at a temperature of about 85° F., and is returned through conduit **45** to the second stage of compressor **22** for recompression and recycling in the system.

Simultaneously, the remaining third of the high pressure stream flowing into junction **33** flows out through channel *a* of heat exchanger **37**, where it is cooled to a temperature of, say, −287° F. by counterflowing streams. It flows out of cold exchanger **37** through conduit **47**, and into the throttle valve **48** where it is isenthalpically expanded to a pressure of, say, 40 pounds per square inch absolute, and cooled to a temperature of, say, −303° F. The stream then passes into a first separator **51** through conduit **49**, where the liquid portion is separated out, and the vapor phase passes out of the top of the vessel through conduit **59** to join the medium-low pressure gas stream flowing into junction **42** for return through the heat exchangers.

The liquid **52** from the bottom of separator **51** passes out through conduit **53** and through a second isenthalpic expansion step in throttle valve **54**, where it is expanded to a pressure of, say, 19 pounds per square inch absolute at a temperature of, say, −316° F. The fluid from this second expansion step flows into a second separator **55**, in which the liquid **56** is collected in the bottom, from which the liquid product is withdrawn through outlet valve **57**. The low pressure flash gas from this separator passes out through the top of the vessel through conduit **58**, channel *c* of cold-leg heat exchanger **37**, connecting conduit **62**, channel *c* of heat exchanger **28**, and conduit **63**. The latter joins junction **21** at the inlet to the system, where the low pressure stream, warmed to about 85° F., and at a pressure of 15 pounds per square inch absolute, joins the incoming make-up stream for recompression and recycling through the system.

A combined air separation and liquefaction system will now be described in greater detail, which includes a nitrogen liquefaction cycle substantially similar to that described with reference to FIGURE 5, with several slight

modifications whereby a portion of liquid nitrogen stream serves as refrigerating reflux in the low pressure column of the air separation system, and provides refrigeration for condensing flash vapor rising off of the liquid oxygen storage tank.

Referring now to FIGURES 6 and 7 of the drawings, which fit together in the manner indicated by FIGURE 8, there is shown, in detailed schematic, a combined air separation, oxygen and nitrogen liquefaction system, illustrative of the principles of the present invention.

For the purposes of the present illustration, a separation-liquefaction system will be described which is designed to produce liquid oxygen at the rate of 100 tons per day and liquid nitrogen at the rate of 304 tons per day.

Referring to FIGURE 6 which shows the air separation unit, air flowing at the rate of about 8,000 standard cubic feet per minute, a temperature of 90° F., and at atmospheric pressure, is introduced through a conventional, non-lubricated type of fiberglas air filter **71** to the suction inlet of a conventional oil-free compressor **72**, where the air is compressed to about 110 pounds per square inch absolute. Compressor **72**, in the present example, is a three-stage integral-gear centrifugal compressor with full cooling.

After compression, the air stream passes through aftercooler **73**, where it is water cooled to a temperature of about 95° F., and thence through water separator **74**, from which it flows through a refrigerator **76**, consisting of a refrigeration circuit **75** which employs one of the fluorocarbon refrigerants. This unit operates to bring the temperature of the stream down to 40° F. The stream then passes through another water separator **77** to junction **78** where the stream passes through a pair of conventional drying chambers **79** and **81**, where it is dried to a very low dew point.

The dried stream then passes at a pressure of 96 pounds per square inch absolute through conduit **82** to the channel *a* of a heat exchanger **83** where the temperature is reduced to —125° F. by counterflowing streams of air and nitrogen. In the present example, this heat exchanger is a conventional type, consisting of brazed aluminum cores.

Carbon dioxide impurity and any remaining water vapor are removed from the stream as it passes from the junction **84** through the dual-bed absorption chambers **85** and **86**, adapted for low temperature removal of carbon dioxide by means of absorbing materials such as the zeolites, known in the art as molecular sieves. The unit is adapted to be reactivated every 16 hours using low-pressure cycle nitrogen. The air stream then passes at a pressure of about 90 pounds per square inch absolute through channel *a* of a second heat exchanger **89**, where the temperature is reduced to —287° F.

At the aforesaid temperature and at a pressure of about 89 pounds per square inch absolute, the stream enters into the bottom of the high pressure rectification column **91**, which in the present illustration is a conventional type. The air is separated by distillation in column **91** into a bottom liquid product containing about 38% oxygen, which in the specification hereinafter will be referred to as "rich liquid." Pure nitrogen gas at the top of column **91** passes out through the outlet pipe **113** and into the reboiler **106**, where it is condensed by heat exchange with evaporating liquid oxygen from the bottom of low pressure column **103**.

About 60% of the pure liquid nitrogen from reboiler **106** passes back into the top of high pressure column **91** through inlet pipe **115**, where it is used for reflux, while the remainder (3,400 standard cubic feet per minute) passes into coil **116** of the subcooler **95**, which in the present example is a wound tube aluminum exchanger having three tube passes and a single shell pass. In subcooler **95** this liquid nitrogen is subcooled by cold low-pressure nitrogen gas passing in the outer shell, to a temperature of —305° F., at a pressure of 80 pounds per square inch absolute, before it passes to junction **118**, under control of valve **120**, and through inlet **119** into the top of low-pressure rectification column **103**, where it serves as reflux.

The rich liquid flows out of the bottom of the high pressure rectification column **91** through conduit **93** at the rate of 4,680 standard cubic feet per minute, at a temperature of —278° F., and a pressure of 89 pounds per square inch absolute, through coil **94** of subcooler **95**, and through the junction **96** into the silica gel absorber **97–98**, where hydrocarbon impurities, such as acetylene, are removed before it passes through valve **101** and through inlet **102** entering as a feed-stream into the low pressure column **103**, at a point part-way up in the column.

The final separation of oxygen and nitrogen occurs in the low pressure column **103**, where all of the air is separated into pure products except for a small control stream. The latter serves to stabilize operation of the column, passing out through outlet pipe **133** at the rate of 321 standard cubic feet per minute, a temperature of —307° F., and a pressure of 20 pounds per square inch absolute. This stream ultimately passes through heat exchanger column **89***d*, connecting pipe **134**, and column *d* of heat exchanger **83**, to outlet **135**, where it is vented to the atmosphere at about 36° F.

As previously pointed out, reflux for low pressure column **103** is supplied by condensed liquid nitrogen from high pressure column **91** through valve **120**. This is augmented for refrigeration purposes by a stream of liquid nitrogen flowing from the nitrogen liquefaction unit through conduit **122** under control of valve **123**. In the present example, this stream flows at the rate of 2,066 standard cubic feet per minute, at a temperature of —303° F., and a pressure of 40 pounds per square inch absolute. It will be apparent that valves **120** and **123** will regulate the respective flows to provide the desired degree of refrigeration in the reflux stream.

Pure liquid oxygen flows out of the bottom of the low pressure column **103**, through conduit **104** and into junction **105**, where a portion passes through the column *b* of the reboiler **106** where it is evaporated by heat exchange with condensing liquid nitrogen from the high pressure rectifying column **91**, and passes back into low pressure column **103**, through inlet **107** at the lower end.

Liquid oxygen product from the low pressure column **103**, flowing at the rate of 1,676 standard cubic feet per minute, at a temperature of —289° F., and a pressure of 23 pounds per square inch absolute, is pumped out of junction **105** by means of pump **109** through the coil **110** of subcooler **95**, where it is reduced to a temperature of —299° F. at a pressure of 40 pounds per square inch absolute, and ultimately through conduit **111** to the liquid oxygen storage tank **112**, shown in FIGURE 7.

Pure nitrogen from the top of low pressure column **103** passes out through vent **124**, at the rate of 8,159 standard cubic feet per minute, a temperature of —316° F. and pressure of 19 pounds per square inch absolute. It flows through the outer shell of subcooler **95**, cooling the liquids passing through the inside coils, and then flows through conduit **126** at a temperature of —283° F. to channel *b* of heat exchanger **89**, connecting conduit **127** and channel *b* of heat exchanger **83**, where the temperature is raised to 36° F. at 15 pounds per square inch absolute pressure. From here it passes through conduit **128** as the make-up stream for the nitrogen liquefaction cycle, to be described presently

Pure oxygen vapor passes through conduit **130** at the lower end of low pressure column **103**, at a temperature of —289° F. and a pressure of 23 pounds per square inch absolute, through channel *c* in each of heat exchangers **89** and **83**, and is vented into the atmosphere through vent **132**

An auxiliary path is provided between the high pressure column **91** and the low pressure column **103**,

through outlet **136** at the lower end of column **91** so that a portion of the cooled air stream, about 25% or less, coming into the lower end of column **91** can be withdrawn if desired under control of valve **137**, partially rewarmed in channel *e* of heat exchanger **89**, expanded with the production of work in expander **139**, and introduced into low pressure column **103** at a point below the middle, through inlet **142** under control of valve **141**. This auxiliary path provides means, if desired, for saving power in the refrigeration system, at the expense of lower oxygen recovery and lower purity by the nitrogen product.

Referring now to FIGURE 7, this shows a schematic diagram in accordance with the present invention of a nitrogen liquefaction circuit to which the make-up stream of gas is furnished through conduit **128**. In the present example, the following is a typical analysis of the impurity content of the nitrogen make-up stream:

| | P.p.m. |
|---|---|
| Oxygen | 3 |
| Argon | 500 |
| Carbon dioxide | <1 |
| Hydrocarbon ($C_2H_4$) | <1 |
| Helium | <10 |
| Neon | <10 |
| Water vapor | <1 |

In the example under description, which anticipates a liquid nitrogen output of 304 tons per day, the stream of nitrogen flows from conduit **128** into the junction **129** at the rate of 8,159 standard cubic feet per minute, a temperature of 36° F., and a pressure of about 15 pounds per square inch absolute.

The valve **149** can be utilized to control the rate of flow of gas from the junction **129**. In the present example, gas flows at the rate 7,998 standard cubic feet per minute from junction **129** into junction **150**, at a temperature of 36° F., and a pressure of 15 pounds per square inch absolute. The low pressure nitrogen stream returning through conduit **221** flows into junction **150** at the rate of 637 standard cubic feet per minute, a temperature of 85° F., and a pressure of 15 pounds per square inch absolute.

The low pressure stream flows out of junction **150** to the first compression stage **151** at the rate of 8,535 standard cubic feet per minute, at a temperature of 50° F., and pressure of 15 pounds per square inch absolute, which is raised to approximately 32 pounds per square inch absolute in the first stage. The stream from the first stage is cooled down in after-cooler **152**, and flows into junction **201**, where it is joined by the medium pressure return stream flowing through conduit **199** at the rate 25,665 standard cubic feet per minute, at a temperature approximating 85° F., and pressure of 32 pounds per square inch absolute.

The fully compressed nitrogen then flows through the rate of 34,200 standard cubic feet per minute through four additional stages of compression, **153**, **155**, **157**, and **159**, each followed by a respective after-cooler **154**, **156**, **158**, or **160**. The stream emerges from the fifth compression stage and its after-cooler into conduit **162** at a pressure of 430 pounds per square inch absolute and a temperature of 95° F.

The compressors **151**, **153**, **155**, **157**, and **159** are conventional types which are operated in series from a common 10,000 horsepower motor, and controlled by means of suction-throttling and discharge pressure control. Reverse rotation is prevented by a check valve installed in the discharge line. The intercoolers and after-coolers **152**, **154**, **156**, **158**, and **160** are conventional types of water coolers.

The partially compressed stream passes through conduit **162** to a series-connected pair of centrifugal compressors, of conventional form, in which the stream is compressed in two steps to 670 pounds per square inch absolute, at a temperature of 95° F. Each of these compressors is followed by a conventional after-cooler, **164** and **167** respectively. Moreover, the centrifugal compressors are respectively coupled to a pair of expansion turbines **194** and **188**, which are mounted on the same shaft, in such a manner that the compressor wheels serve as a brake for the turbines, absorbing the work of the expanding gas.

The fully compressed nitrogen then flows through the conduit **168** into channel *a* of heat exchanger **169** for cooling by the outgoing low pressure and medium pressure nitrogen recycle streams. This heat exchanger is a brazed aluminum type comprising five cores in parallel flow.

At the point in channel *a* of exchanger **169** where the high pressure nitrogen stream reaches −40° F., the total stream is withdrawn from the heat exchanger **169** through conduit **170** and passed into a conventional refrigeration unit **175** where it is cooled from −40° F. to −101° F.

In the present example, the refrigeration system **175** comprises two different refrigeration cycles operating in cascade to cool the high pressure nitrogen stream. The first of these refrigeration cycles employs dichlorodifluoromethane $CCl_2F_2$, known by the trade-name "Freon 12"; and the second cycle employs monochlorotrifluoromethane, known by the trade-name "Freon 13." (Both of these are registered tradenames of E. I. du Pont de Nemours and Company.) The nitrogen stream emerging at −40° F. from channel *a* of heat exchanger **169** flows through conduit **170** under a pressure of 669 pounds per square inch absolute, at the rate of 34,200 standard cubic feet per minute into the refrigeration unit **175**.

After the cooled nitrogen stream has returned from refrigeration unit **175** to channel *a'* of heat exchanger **169** at a temperature of −101° F., it is further cooled by the counter-flowing fluids in channels *b* and *c* thereof to −130° F. at which temperature and a pressure of 663 pounds per square inch absolute it leaves the heat exchanger **169** and flows into junction **186**. At this point approximately 70% of the high pressure nitrogen stream (24,200 standard cubic feet per minute) is drawn off into conduit **187**. This major portion passes into turboexpander **188**, where it is expanded with the production of work to a pressure of 147 pounds per square inch absolute, and is thereby cooled to a temperature of −236° F. As pointed out previously turboexpander **188**, and its companion, turboexpander **194**, used in the next stage, are of the radial inflow type. These turboexpanders are mounted on the same shaft with and drive the respective centrifugal compressors **166** and **163**; they are lubricated by a common system. Variable inlet nozzles control the flow through the turboexpanders which regulates the power available to compress the cycled nitrogen.

The stream, expanded to 147 pounds per square inch absolute, passes out of turboexpander **188** through conduit **189** and is reheated in channel *d* of heat exchanger **192** to a temperature of −213° F. The stream is then again expanded with the performance of work through a second stage comprising the turboexpander **194** from a pressure of 145 to a pressure of 35 pounds per square inch absolute and is cooled to a temperature of −289° F. The medium-low pressure stream passes out of turboexpander **194** through conduit **195** and into junction **196**, where it re-enters channel *b* of heat exchanger **192** through conduit **197**, in combination with the return medium-low pressure flow through conduit **210**. The combined streams pass through conduit **197** into channel *b* of heat exchanger **192**, and through conduit **198** into channel *b* of heat exchanger **169**, where they are heated up to a temperature of 85° F. Flowing at the rate of 25,665 standard cubic feet per minute, the stream then passes through conduit **199** and into the suction end of the second compression stage, through junction **201**, at a

pressure of 32 pounds per square inch absolute for recycling in the liquefaction system.

The approximately 30% of the high pressure stream remaining at junction **186**, where the major portion was diverted through the turboexpanders, passes through channel *a* of heat exchanger **192**, where it is cooled to a saturated fluid of a single phase at about —269° F. This product stream, flowing at the rate of approximately 10,000 standard cubic feet per minute in conduit **203**, and at a pressure of 660 pounds per square inch absolute, is throttled (isenthalpically expanded) to 19 pounds per square inch absolute in two steps. The stream is first expanded through Joule-Thompson expansion valve **204**, which is a conventional cryogenic throttle-valve, to approximately 40 pounds per square inch absolute, at a temperature —303° F. This fluid passes into vessel **206** atop the liquid oxygen storage tank **112**. Vessel **206**, which is a conventional type of liquid separator, serves as a liquid-vapor separator as well as a condenser for flash oxygen vapor from the tank, which flows back into the oxygen tank through receptacle **206***a*.

The nitrogen flash gas passing out of the top of separator **206**, moves through conduit **210** to junction **196**, flowing at the rate of 1,465 standard cubic feet per minute, at a temperature of —303° F., and a pressure of 36 pounds per square inch absolute. The combined low pressure stream then passes through channel *b* of each of the exchangers **192** and **169**, joining the suction portion of the second compression stage at 85° F., as previously described.

The liquid fraction of nitrogen passes out of separator **206** through conduit **207**, and into junction **121**, flowing at the rate of 8,535 standard cubic feet per minute, at a temperature of —303° F., and pressure of 40 pounds per square inch absolute. Part of the liquid nitrogen serves as refrigerating reflux for the low pressure column **103** of the air separation system, passing through conduit **122** at the rate 2,066 standard cubic feet per minute. The remainder (flowing at the rate of 6,469 standard cubic feet per minute) passes through conduit **208** to a second Joule-Thompson expansion valve **209**, where it is again throttled (isenthalpically expanded) to a pressure of 19 pounds per square inch absolute, and a temperature of —316° F. It flows into a second separator **211** at the rate of 6,469 standard cubic feet per minute, where the liquid nitrogen separates out and is expanded into the storage tank **214** at a pressure of 15 pounds per square inch absolute through valve **213**. Both the liquid oxygen storage tank **112** and liquid nitrogen storage tank **214**, are conventional insulated types of a form well-known in the art.

Saturated nitrogen vapor flows out of separator **211** at the rate of 430 standard cubic feet per minute, a temperature of —316° F., and a pressure of 19 pounds per square inch absolute, through conduit **215** to junction **218** where it is joined by flash nitrogen vapor from storage tank **214**, pumped through conduit **216** by a conventional cold blower pump **217**, at a rate of 207 standard cubic feet per minute, a temperature of —303° F., and a pressure of 19 pounds per square inch absolute. The combined low pressure stream passes through conduit **219** and channel *c* of heat exchanger **192**. It then passes through conduit **220** to channel *c* of heat exchanger **169**, where it emerges at a temperature of 85° F., flowing through conduit **227** into junction **150** at a rate of 637 standard cubic feet per minute and at a pressure of 15 pounds per square inch absolute, through which it returns to the first compression stage for recycling in the nitrogen liquefaction system.

It will be apparent to those skilled in the art that this invention is not limited to the specific embodiments disclosed by way of illustration; but rather, that the scope of the invention is defined in terms of the appended claims.

We claim:

**1.** In a cycle for the liquefaction of low boiling gas which comprises the steps of:

compressing a primary stream including the feed stream of said gas to a head pressure not exceeding about two and one-half times the critical pressure of said gas,

cooling said compressed primary stream through a first cooling step in a first heat exchanger,

further cooling at least a portion of said compressed primary stream through a second cooling step in a second heat exchanger, without substantial liquefaction thereof,

isenthalpically expanding said compressed portion after said second cooling step to a low pressure to form a liquid fraction and a remaining vapor fraction, and

returning the remaining low pressure vapor fraction of said portion at said low pressure for recompression and recycling through a path including said heat exchangers in countercurrent with streams being cooled including said compressed portion;

the improvement which comprises:

separating said compressed primary stream before said second cooling step into a major portion and a minor portion, whereby the compressed portion further cooled in said second heat exchanger is said minor portion,

withdrawing and expanding said major portion through a plurality of work expansion steps wherein said major portion is cooled and expanded to a medium-low pressure without liquefaction,

each of said work expansion steps being separated by an intervening reheat step wherein the stream comprising said major portion is warmed up in said second heat exchanger in countercurrent with streams being cooled including said compressed minor portion,

and after said final work expansion step, returning said major portion at a medium-low pressure without liquefaction through said heat exchangers in countercurrent with streams being cooled including said compressed minor portion, for recompression and recycling.

**2.** In a cycle for the liquefaction of low boiling gas in accordance with claim **1**, expanding said major portion through two work expansion steps separated by one intervening reheat step wherein the stream comprising said major portion is warmed in countercurrent with said minor portion being cooled.

**3.** A cycle for the liquefaction of low boiling gas in accordance with claim **1** wherein said step of compressing said primary stream of gas takes place in a plurality of stages, wherein said low pressure vapor fraction is returned to the initial compression stage for recompression and recycling, and wherein said medium-low pressure major portion is returned to a later compression stage for recompression and recycling.

**4.** In a cycle for the liquefaction of low boiling gas which comprises

compressing a primary stream of said gas to a head pressure not exceeding about two and one-half times the critical pressure of said gas,

cooling said compressed primary stream through a first cooling step,

further cooling at least a portion of said compressed primary stream through a second cooling step in heat exchanger means, wherein an inflected cooling characteristic is produced in said heat exchanger,

isenthalpically expanding said compressed and further cooled portion to a low pressure to form a liquid fraction and a remaining vapor fraction,

and returning the remaining low pressure vapor fraction of said portion for recompression and recycling through a path including said heat exchanger means

in countercurrent with the stream being cooled comprising said compressed portion;

the improvement which comprises:

separating said compressed primary stream before said second cooling step into a major portion and a minor portion, whereby the portion further cooled in said heat exchanger means is said minor portion,

withdrawing and expanding said major portion through a plurality of work expansion steps, cooling and expanding said major portion to a medium-low pressure without liquefaction,

each of said work expansion steps being separated by an intervening reheat step wherein the stream comprising said major portion is warmed up in said heat exchanger means in countercurrent with streams being cooled including said compressed minor portion,

and following said final work expansion step, returning said major portion at medium-low pressure without liquefaction through said heat exchanger means in countercurrent with streams being cooled including said minor portion for recompression and recycling,

thereby producing a composite warming characteristic which approximates the inflected shape of the cooling characteristic of the stream comprising said compressed portion.

5. A cycle for liquefying nitrogen gas which comprises the steps of

compressing a primary stream of nitrogen including a feed stream through a plurality of compression stages to an elevated pressure within the range 40 to 75 atmospheres,

cooling said compressed primary stream by means including a first heat exchanger to a temperature within the range —120° F. to —130° F.,

subsequently separating said compressed primary stream into a major stream consisting of between 65 and 75% by volume of said primary stream, and a minor stream consisting of the remainder,

further cooling said compressed minor stream through a second heat exchanger,

isenthalpically expanding said compressed minor stream to a low pressure to form a liquid fraction and a remaining vapor fraction,

returning the remaining low pressure vapor fraction through said heat exchangers in countercurrent with streams being cooled including said compressed minor stream for recompression and recycling,

expanding said compressed major stream through a plurality of work expansion steps wherein said major stream is cooled and expanded to a medium-low pressure without liquefaction,

each of said work expansion steps being separated by a reheat step wherein said major stream is warmed up in said second heat exchanger in countercurrent with said cooling compressed minor stream,

and after said final work expansion step returning said major stream at a medium-low pressure without liquefaction for recompression and recycling through a path including said heat exchangers in countercurrent with streams being cooled including said compressed minor stream.

6. A cycle for the liquefaction of nitrogen in accordance with claim 5

wherein said major stream is expanded through a first work expansion step to a pressure less than a quarter of said elevated pressure and a temperature within the range —235° F. to —245° F.,

said major stream is subsequently reheated in said second heat exchanger in countercurrent with said compressed minor portion to a temperature within the range —210° F. to —220° F.,

and said major stream is finally expanded in a second work expansion step to a pressure slightly in excess of 2.5 atmospheres and cooled to a temperature within the range —285° F. to —305° F.,

prior to returning without liquefaction through said heat exchangers.

7. In a cycle for the liquefaction of nitrogen in accordance with claim 5 wherein said step of compressing said primary stream takes place in a plurality of stages, wherein said low pressure vapor fraction is returned to the initial compression stage for recompression and recycling, and wherein said medium-low pressure major portion is returned to a later compression stage for recompression and recycling.

8. A cycle for the liquefaction of nitrogen in accordance with claim 5 wherein said compressed primary stream is initially cooled in said first heat exchanger to a temperature within the range —35° F. to —45° F.,

said compressed cooled primary stream is then withdrawn laterally from said heat exchanger and cooled by external refrigeration means to a temperature within the range —95° F. to —105° F.,

and said further cooled primary stream is again passed into said first heat exchanger where it is cooled to a temperature within the range —120° F. to —130° F. by heat exchange with counterflowing streams in said heat exchanger.

9. In an air separation and liquefaction cycle which comprises in combination the steps of:

removing impurities from a feed-stream of said air including carbon dioxide and water,

compressing said feed-stream to an elevated pressure,

cooling said feed-stream to approximately its saturation temperature by heat exchange with outgoing gas streams,

separating said feed-stream by distillation in a high pressure rectification column into a bottom product called rich liquid containing substantially more than 20% by volume of oxygen and an overhead high purity nitrogen product,

subcooling and further separating said rich liquid by distillation in a low pressure rectification column into a high purity liquid oxygen product and an overhead high purity nitrogen product,

condensing the nitrogen product of said high pressure rectification column by reboiling said liquid oxygen product from the bottom of said low pressure rectification column,

utilizing a major portion of said condensed liquid nitrogen product as reflux for said high pressure rectification column,

subcooling and utilizing the remainder of said condensed liquid nitrogen product for reflux in said low pressure rectification column,

storing the liquid oxygen product of said low pressure rectification column in an insulated storage vessel,

passing a stream of high purity nitrogen gas overhead from said low pressure rectification column through subcooling means for concurrent streams of rich liquid oxygen and liquid nitrogen,

utilizing said stream of high purity nitrogen as a feed-stream for a liquefaction cycle operating in conjunction with said air separation cycle,

compressing and cooling nitrogen feed-stream through a first cooling step in a first heat exchanger,

further cooling at least a portion of said compressed nitrogen feed-stream through a second cooling step in a second heat exchanger without substantial liquefaction thereof,

isenthalpically expanding said compressed nitrogen portion after said second cooling step to a low pressure to form a liquid fraction and a remaining vapor fraction, and

separating and returning the remaining low pressure vapor fraction of said portion at said low pressure for recompression and recycling through a path in-

cluding said heat exchangers in countercurrent with streams being cooled including the compressed nitrogen feed-stream;

the improvement which comprises:

separating said compressed nitrogen feed-stream before said second cooling step in said nitrogen liquefaction cycle into a major portion and a minor portion whereby the compressed portion further cooled in said heat exchanger is said minor portion,

withdrawing and expanding said major portion through a plurality of work expansion steps wherein said major portion is cooled and expanded to a medium-low pressure without liquefaction,

each of said work expansion steps being separated by an intervening reheat step, wherein the stream comprising said major portion is warmed up in said second heat exchanger in countercurrent with streams being cooled including said compressed minor portion,

after said final work expansion step returning said major portion at a medium-low pressure without liquefaction through said heat exchangers in countercurrent with streams being cooled including said minor portion for recompression and recycling,

utilizing a heat exchange between oxygen vapor rising off of said insulated storage vessel in said air separation system and said isenthalpically expanded nitrogen portion for separating liquid and vapor in said portion and for recondensing said oxygen vapor to liquid,

and utilizing at least a portion of the liquid fraction of said nitrogen to supply refrigerating reflux to said low pressure rectification column in said air separation cycle.

**10.** An air separation cycle in combination with oxygen and nitrogen liquefaction cycles which comprises the steps of:

compressing a feed-stream of said air,

cooling said compressed stream of air through a path including heat exchanger means,

passing said cooled compressed stream of air into a high pressure rectification column for separation into rich liquid in the bottom of said column comprising substantially more than 20% by volume of oxygen, and nitrogen gas in the top of said high pressure column,

further cooling said rich liquid derived from the bottom of said high pressure rectification column in a subcooler in a heat exchange with counterflowing cold nitrogen vapor,

introducing said cooled rich liquid part-way up in a second low pressure rectification column,

passing the nitrogen vapor from the top of said high pressure rectification column through a condenser for condensation in a heat exchange with counterflowing liquid oxygen,

returning one portion of said condensed liquid nitrogen to the top of said high pressure column for refluxing,

and passing another portion of said liquid nitrogen through said subcooler in countercurrent with cooled nitrogen vapor and into the top of said low pressure rectification column for refluxing,

passing purified liquid oxygen out through the bottom of said low pressure column,

vaporizing part of said liquid oxygen in said condenser in a heat exchange with cold nitrogen vapor from the top of said high pressure rectification column and passing said oxygen vapor into said low pressure column,

pumping part of said liquid oxygen through said subcooler for further cooling and into an insulated receptacle for storage,

returning a control stream of cold low pressure nitrogen from near the top of said low pressure rectification column through said heat exchanger means in countercurrent with high pressure cooling streams, and ultimately releasing said stream to the atmosphere,

returning a stream of cold oxygen vapor from near the bottom of said low pressure rectification column through said heat exchanger means and releasing said stream into the atmosphere,

returning a stream of purified cold nitrogen from the top of said low pressure rectification column, and through said subcooler and heat exchanger means to said nitrogen liquefaction cycle as the make-up stream therefor,

in said nitrogen liquefaction cycle compressing said nitrogen stream through a plurality of compression stages terminating in at least one centrifugal compressor stage,

passing said compressed nitrogen make-up stream into a first heat exchanger for cooling to a temperature within the range —35° F. to —40° F.,

withdrawing said compressed nitrogen stream laterally from said first heat exchanger and passing it through refrigeration means comprising at least one external refrigerating cycle, wherein said nitrogen make-up stream is cooled to a temperature within the range —95° F. to —105° F.,

again passing said compressed cooled nitrogen stream into said first heat exchanger for cooling to a temperature within the range —120° F. to —130° F.,

separating said compressed nitrogen stream into a major stream consisting of 65% to 75% by volume of the flow of said compressed nitrogen stream, and a minor stream consisting of the remainder,

withdrawing said major compressed nitrogen stream through a first expansion turbine wherein said stream is work-expanded to a pressure within the range 140 to 150 pounds per square inch absolute and cooled to a temperature within the range —235° F. to —245° F.,

reheating said major stream to a temperature within the range —210° F. to —220° F. in a second heat exchanger in countercurrent with said compressed minor stream,

re-expanding said major stream through a second expansion turbine wherein said stream is work-expanded to a medium-low pressure within the range 30 to 40 pounds per square inch absolute, and cooled to a temperature within the range —285° F. to —305° F.,

returning said medium-low pressure stream through said heat exchangers to a stage following the initial stage of said compression for recompression and recycling,

passing said minor compressed nitrogen stream through said second heat exchanger in countercurrent with said low pressure returning major stream and thereby cooling said minor stream to a temperature within the range —260° F. to —270° F. at a pressure within the range 650 to 11,000,

expanding said cooled compressed minor stream in a first isenthalpic expansion step through a throttle valve to a pressure slightly above two atmospheres, thereby to convert a fraction of said stream to liquid,

separating out the nitrogen liquid fraction from the nitrogen vapor fraction in a heat exchange with flash oxygen vapor in condensing means communicating with said insulated receptacle for storing liquid oxygen from said air separation system,

returning the medium-low pressure vapor fraction from said first isenthalpic expansion step through said heat exchanger, together with the medium-low pressure stream from said expansion turbine, to a stage following the initial stage of said compressor for recompression and recycling,

making a portion of said nitrogen liquid fraction available for use as a reflux in the top of the low pressure rectification column in said air separation system,

passing the remainder of the nitrogen liquid fraction resulting from said first isenthalpic expansion step into a valve for a second isenthalpic expansion step to a pressure slightly above atmospheric pressure and a temperature below the liquefaction temperature of nitrogen,

separating off the low pressure saturated nitrogen vapor fraction from the final liquid nitrogen fraction resulting from said second isenthalpic expansion step in another separating means, which includes flash nitrogen vapor from liquid nitrogen stored in said cycle,

passing said low pressure nitrogen vapor through said heat exchangers in countercurrent with cooling high pressure streams to the initial compression stage of said nitrogen liquefaction cycle for recompression and recycling,



and drawing off said final liquid nitrogen fraction for storage in an insulated receptacle.

**11.** An air separation cycle in combination with oxygen and nitrogen liquefaction cycles in accordance with claim **10**, wherein at least one said centrifugal compressor stage in said nitrogen liquefaction cycle is run on power derived from said expansion turbine, in said cycle.

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NORMAN YUDKOFF, *Primary Examiner.*

W. PRETKA, *Assistant Examiner.*

# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,358,460 December 19, 1967

Donald L. Smith et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, lines 56 and 57, for "The fully compressed nitrogen then flows through the rate of" read -- The augmented stream flows out of junction 201 at the rate of --; column 15, line 2, for "as a reflux" read -- as reflux --.

Signed and sealed this 10th day of June 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents