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C. J. SCHILLING ETAL

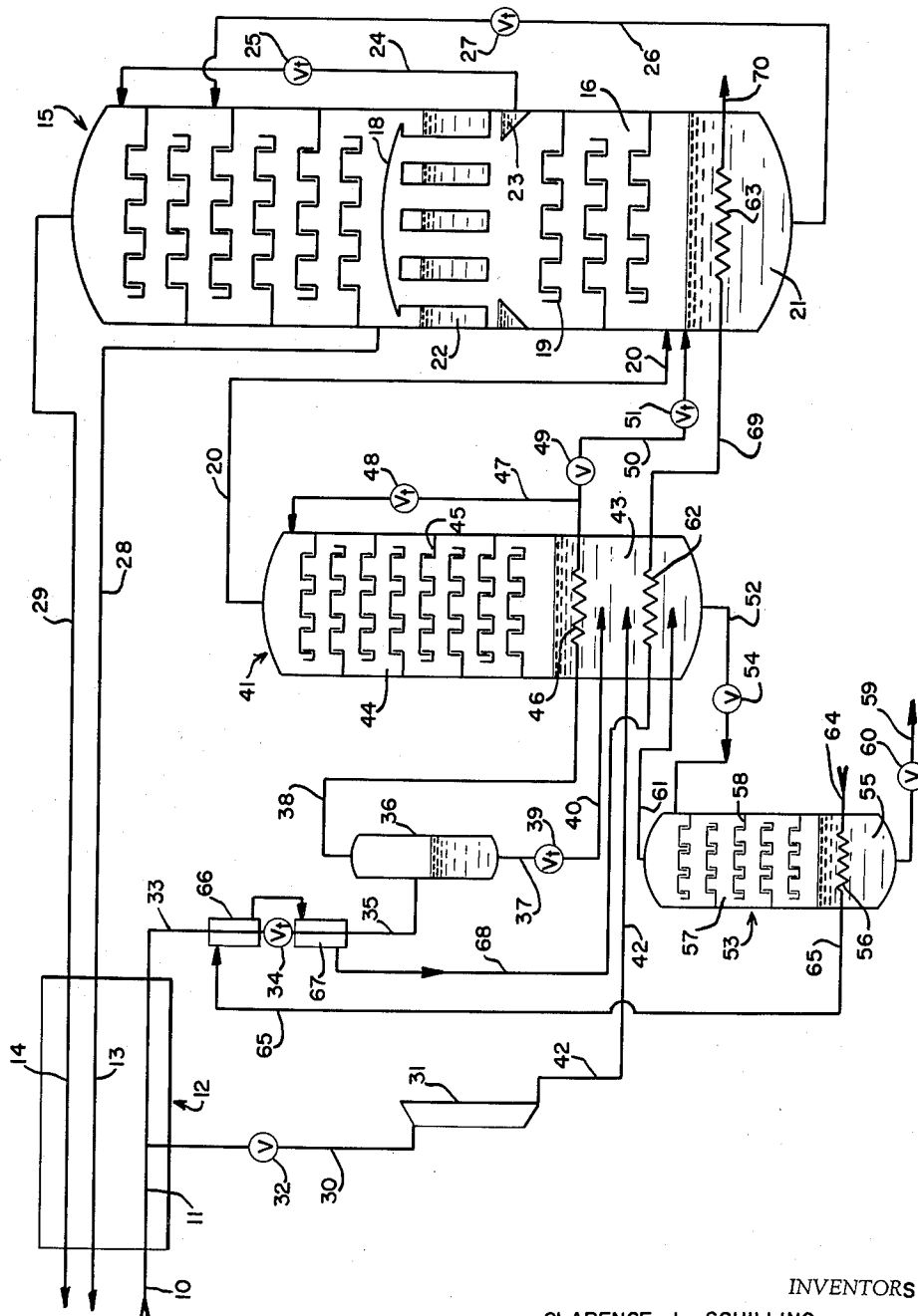
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METHOD AND APPARATUS FOR FRACTIONATING GASEOUS MIXTURES

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Fig. 1.



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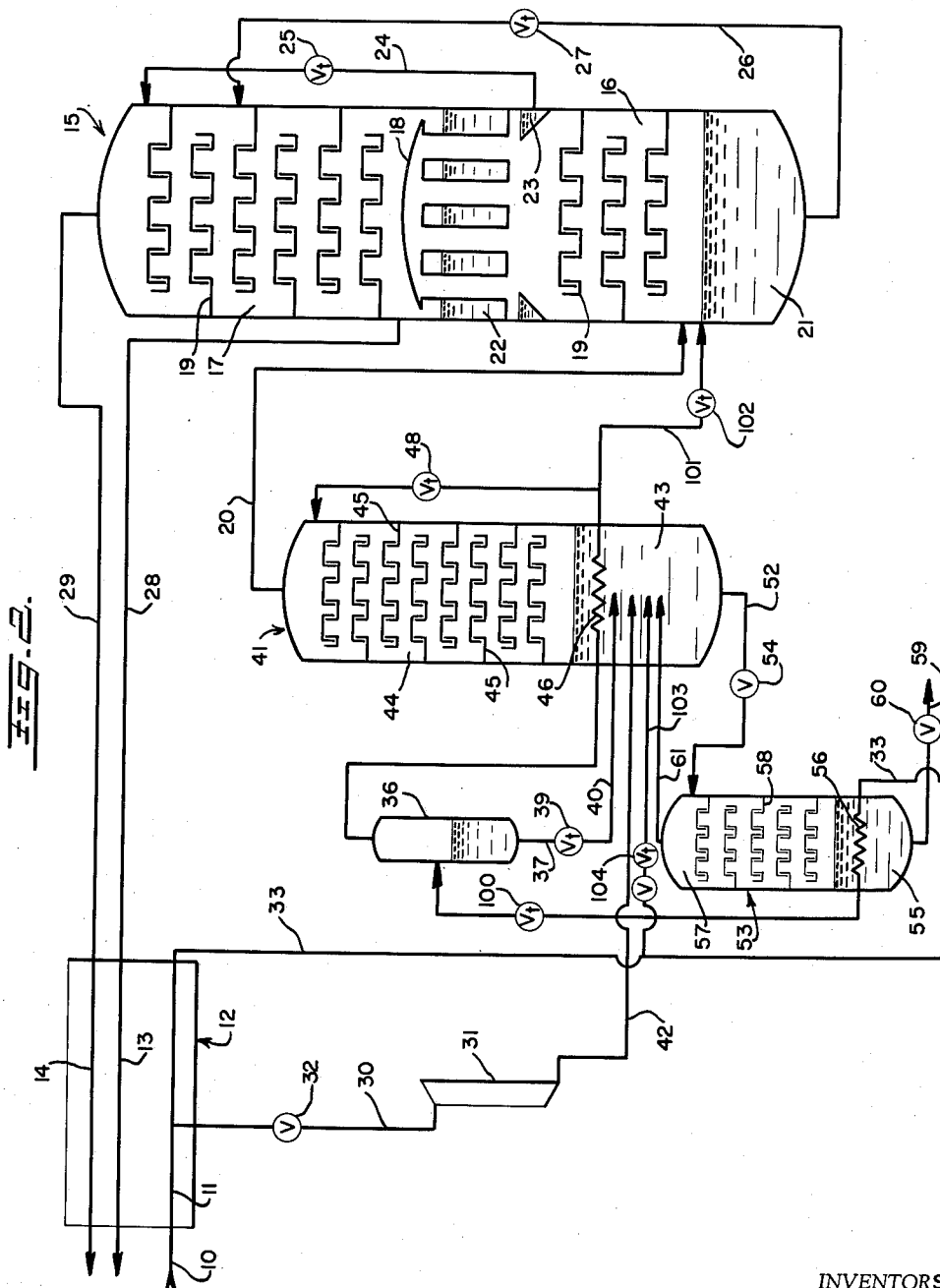
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3 Sheets-Sheet 2



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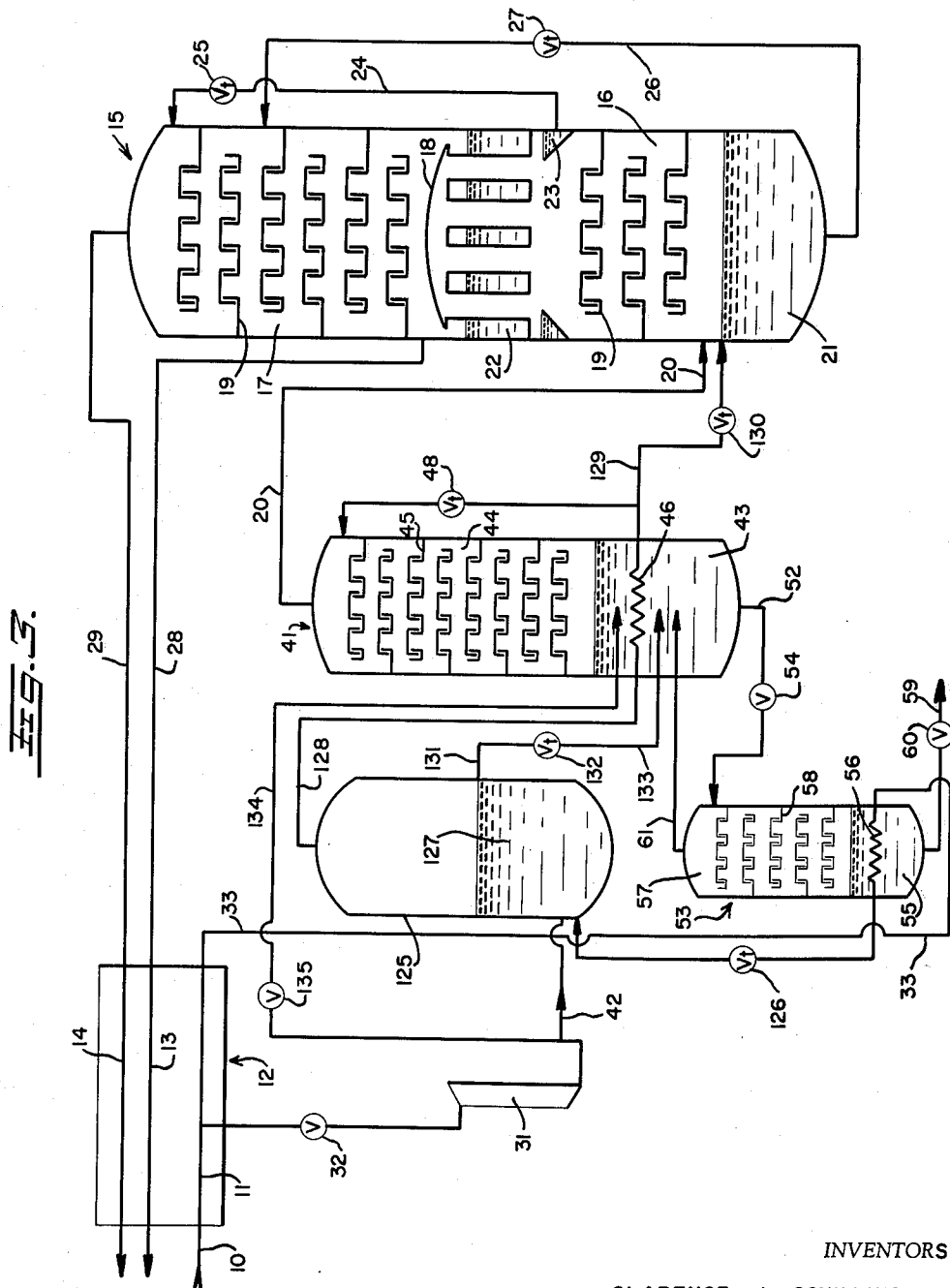
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METHOD AND APPARATUS FOR FRACTIONATING GASEOUS MIXTURES

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17 Claims. (Cl. 62—25)

This invention relates to separation of gaseous mixtures and more particularly to methods of and apparatus for separating gaseous mixtures by a low temperature fractionating operation in which high boiling point impurities are removed from the gaseous mixture prior to the fractionating operation.

Gaseous mixtures separated into components by low temperature fractionating operations invariably contain in addition to the desired low boiling point components certain high boiling point materials usually in gaseous phase at atmospheric temperature and pressure which if not removed from the gaseous mixture prior to entry into the fractionating operation will collect therein and materially affect performance of the fractionating operation or present serious hazards. For example, atmospheric air in addition to the low boiling point components, primarily oxygen and nitrogen, includes moisture, carbon dioxide and other high boiling point components, particularly hydrocarbons. Moisture and carbon dioxide may be adequately removed from atmospheric air by chemical treatment, by freezing, or by filtering and adsorbing processes, but difficulties have been experienced when attempting to reliably remove hydrocarbon impurities to the degrees necessary for same, prolonged operations without materially effecting efficiency of the fractionating operation and without requiring expensive equipment having high maintenance costs.

Prior systems designed for removing high boiling point impurities from feed mixtures, such as hydrocarbons from atmospheric air, for the most part rely upon the features of liquefying a portion of the feed mixture and then scrubbing the unliquefied portion with the liquefied portion to concentrate the impurities in the liquefied portion, attempting to remove the impurities from the liquefied portion and then feeding liquefied portion and the vapor portion to a fractionating operation. According to the prior practices, high boiling point impurities may be removed from the scrubbing liquid by the use of filters and adsorbers or by substantially completely vaporizing the liquid to concentrate the impurities in a small body of liquid which is discharged from the cycle. While the prior arrangements materially aid in overcoming the problems occasioned by the presence of high boiling point impurities in feed mixtures, they are subject to certain disadvantages such as high initial and maintenance costs, materially reducing cycle efficiency and the inability to reliably maintain the quantity of high boiling point impurities entering the fractionating operation below a maximum level necessary under most circumstances for substantially continuous operations without presenting a hazardous condition due to accumulations of high boiling point impurities in the fractionating operation.

It is accordingly an object of the present invention to provide a novel method of and apparatus for removing high boiling point impurities from a gaseous feed mixture prior to separation by a low temperature fractionating operation.

Another object is to provide a novel method of and apparatus for removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature operation in which the total high boiling point impurity in the feed mixture is substantially completely

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removed therefrom prior to introduction of the feed mixture into the fractionating operation.

Still another object of the present invention is to provide a novel method of and apparatus for removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature operation requiring gaseous mixture feed in vapor phase or partly in liquid phase.

A further object is to provide a novel method of and apparatus for removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation in which a portion of the feed mixture is expanded with work to a relatively low temperature of the fractionating operation.

A still further object of the present invention is to provide a novel method of and apparatus for removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation so characterized that the quantity of high boiling point impurities entering the fractionating operation may be accurately determined.

In accordance with the broad concept of the present invention, compressed gaseous mixture is cooled and partly liquefied and then separated into a liquid phase portion containing substantially the entire high boiling point impurities in the gaseous mixture and a vapor phase portion substantially free of such impurities. The liquid phase portion containing the impurities is then substantially completely vaporized and the vapor produced by such vaporization is scrubbed by liquefied gaseous mixture substantially free of high boiling point impurities prior to separation by a low temperature fractionating operation. In accordance with another feature liquefied gaseous mixture substantially free of impurities which scrubs the vapor produced by vaporization of the liquid phase portion containing the impurities is obtained by liquefying the impurity free vapor phase portion withdrawn from the separation step and such liquefaction is preferably accomplished by vaporizing at least a part of the liquid phase portion under reduced pressure. Vaporization of the liquid phase portion containing the impurities is preferably accomplished in separate zones in order to concentrate the impurities in a small body of liquid that may be sampled to determine the quantity of impurities in the feed mixture and that may be periodically discharged from the system. Vapor produced in the vaporization zones is scrubbed with liquid gaseous mixture and the zones are preferably arranged in series relationship so that the vapor emerging from the zone from which the concentrated impurities may be withdrawn is scrubbed in the other zone with liquefied gaseous mixture substantially free of impurities along with the vapor produced upon vaporization of liquid in the latter zone.

The present invention is also adapted for use in a cycle in which a portion of the feed mixture is expanded in an expansion engine to the pressure of the fractionating zone. In such cycles the fluid from the expansion engine is scrubbed with liquid containing high boiling point impurities preferably in the vaporization zone fed with impurity free liquefied gaseous mixture so that the effluent from the expansion engine, which may comprise a greater percentage of the total feed mixture and hence introduce a greater quantity of high boiling point impurity into the cycle, is scrubbed with liquid phase portion to be vaporized and thereafter with impurity free liquid.

The novel method and apparatus provided by the present invention makes it possible to determine from analysis of the concentrated liquid the quantity of high boiling point impurities that are introduced into the fractionating operation. It has been determined that in the partial liquefaction of air and subsequent separa-

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tion of the partially liquefied air into its vapor and liquid phase portions that a definite percentage of the high boiling point hydrocarbon impurities, which is substantially the total high boiling point impurities, will be concentrated in the liquid phase portion. In particular, it has been determined that when air is compressed and cooled to effect 50% liquefaction, that upon subsequent phase separation the following ratios of hydrocarbons in the liquid to the similar hydrocarbons in the vapor will exist:

Methane -----	15.4
Acetylene -----	26
Ethane -----	1500
Ethylene -----	5700

Thus, with respect to methane, about 4% of the methane would be in the vapor phase portion and 96% in the liquid phase portion. This relationship may be improved to further decrease the percentage of hydrocarbons retained in the vapor phase portion of liquefying a greater percentage of the gaseous mixture. Furthermore, by partially liquefying and subsequently separating only a portion of the total feed to the fractionating operation, it is possible to further decrease the percentage of high boiling point impurities that may possibly be introduced into the fractionating column. For example, by partially liquefying 25% of the feed mixture with subsequent separation into the liquid and vapor phase portions, only about 1% of the total methane of the feed mixture would enter the fractionating operation. By determining the hydrocarbon content of the concentrated liquid it is possible to determine, knowing what percentage of the feed mixture fed into the column is derived from the vapor phase portion, the exact quantity of high boiling point impurities entering the fractionating column for all possible conditions of the feed mixture. Thus, it is possible by use of the present invention to accurately determine when accumulations of hydrocarbons in the fractionating operation will reach conditions that cannot be tolerated for safe operation.

The foregoing objects and features of the present invention will appear more fully below from the following detailed description considered in connection with the accompanying drawings which disclose several embodiments of the invention. It is to be expressly understood however that the drawings are designed for purposes of illustration only and not as a definition of the invention, reference for the latter purpose being had to the appended claims.

In the drawings, in which similar reference characters denote similar elements throughout the several views:

FIGURE 1 is a diagrammatic representation of a fractionating cycle embodying the principles of the present invention;

FIGURE 2 is a diagrammatic showing of another embodiment of the present invention; and

FIGURE 3 is a diagrammatic representation of a low temperature fractionating cycle according to another embodiment of the present invention.

With reference more particularly to FIGURE 1 of the drawings, a fractionating cycle for separating air is disclosed therein embodying the principles of the present invention. Although the various embodiments of the present invention are disclosed and described in the environment of air fractionating cycles, it is to be expressly understood that the present invention may be employed in connection with fractionating cycles designed for low temperature separation of other gaseous mixtures such as coke oven gas, for example. As shown, a stream of compressed atmospheric air, which has been treated to remove moisture and carbon dioxide by any suitable process not shown, enters the cycle through conduit 10 and is conducted to pass 11 of a heat exchange device 12 for countercurrent heat exchange effecting relation with oxygen and nitrogen component gases flowing

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through heat exchange passes 13 and 14. The oxygen and nitrogen component gases are product gases of a fractionating column 15 which may be of conventional two-stage construction including a high pressure section 16 and a low pressure section 17 separated by a refluxing condenser 18, the high and low pressure sections being provided with conventional liquid-vapor contact means such as bubble plates 19 as shown. The air feed mixture, which has been substantially entirely freed of high boiling point impurities in accordance with the present invention as will be described below, is introduced through conduit 20 into the high pressure section 16 where the air is partly fractionated into liquid low boiling point fraction, crude oxygen, collecting in a pool 21 in the base of the high pressure section and a gaseous high boiling point fraction, pure nitrogen, which flows upwardly into the refluxing condenser and is liquefied therein upon heat exchange effecting relation with liquid oxygen product collecting in a pool 22 in the base of the low pressure section. Liquefied high boiling point fraction flowing downwardly from the refluxing condenser into the high pressure section as reflux and into a pool 23 from which a stream is withdrawn through conduit 24, expanded in valve 25, and introduced into the top of the low pressure section as reflux. Feed for the low pressure section comprises crude oxygen withdrawn from the pool 21 by conduit 26 and introduced at a midpoint of low pressure section following expansion in the valve 27. Gaseous oxygen product is withdrawn from the low pressure section above the liquid oxygen pool 22 through conduit 28 and conducted to pass 13 of the heat exchange device 12, while nitrogen product is withdrawn from the dome of the low pressure section through conduit 29 and conducted thereby to pass 14 of the heat exchange device.

A portion of the air feed is withdrawn from the pass 11 at a medial point along the length of the heat exchange device 12 through a conduit 30 and is conducted to an expansion engine 31 and therein expanded with work to a pressure substantially corresponding to the pressure existing in the high pressure section 16 of the fractionating column, the portion of the air feed being withdrawn from the pass 11 at a temperature level such that liquid is not formed during its expansion in the expansion engine 31 and a control valve 32 is included in the conduit 30 to determine the portion of the total air feed passed to the expansion engine. The remaining portion of the air feed being further cooled in passing throughout the length of the pass 11 in countercurrent heat exchange effecting relation with oxygen and nitrogen products is conducted by conduit 33 to an expansion valve 34 where its pressure is reduced to an intermediate pressure above the pressure existing in the high pressure section 16 and is then discharged through conduit 35 into a phase separator vessel 36. The pressure and temperature conditions existing downstream of the expansion valve 34 are such that the air is partially in liquid phase and upon being discharged into the vessel 36 a phase separation takes place with the liquid phase being withdrawn through conduit 37 and the vapor phase through conduit 38. Due to the solubility characteristics of hydrocarbon impurities in the liquid and vapor phases, as discussed above, substantially the total high boiling point impurity in the portion of the feed mixture passes through the expansion valve 34, is concentrated in the liquid phase portion, withdrawn through conduit 37, and the vapor phase portion in the conduit 38 is substantially entirely free of high boiling point impurities. The liquid phase portion is expanded in valve 39 to the pressure existing in the high pressure section 16 of the column and is introduced by conduit 40 into the base of a vaporizer-scrubber 41, the effluent from the expansion engine 31 being also fed to the vaporizer-scrubber 41 through conduit 42.

The vaporizer-scrubber 41 includes a liquid receiving

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zone 43 at its base and an upper scrubbing zone 44 provided with a plurality of liquid-vapor contact trays 45. The vapor phase portion of feed mixture substantially free of high boiling point impurities is conducted by conduit 38 to a boiling coil 46 located in the liquid receiving zone 43 and is cooled in heat exchange effecting relation with the liquid air in the zone 43 under relatively lower pressure to effect the liquefaction and the liquefied vapor portion is conducted through conduit 47 to the upper end of the scrubbing zone 44 following expansion in valve 48 to the pressure existing in the vaporizer-scrubber 41. Under certain circumstances, such as when starting up the cycle for example, it may be desirable to introduce a portion of the liquefied vapor phase portion directly into the fractionating column as feed. This may be accomplished by opening valve 49 and passing a portion of the liquefied vapor phase portion, which is substantially entirely free of high boiling point impurities, through conduit 50 and expansion valve 51 into the high pressure section 16.

Liquid is withdrawn from the base of the vaporizer-scrubber 41 through conduit 52 and introduced into a vaporizer-scrubber 53, a valve 54 being provided to determine the quantity of liquid withdrawn. The vaporizer-scrubber 53 includes a liquid receiving zone 55 provided with a boiling coil 56 and thus comprises vaporizer means. The vaporizer-scrubber 53 also includes a scrubbing zone 57 having a plurality of liquid-vapor contact trays 58, and may be of smaller capacity than the vaporizer-scrubber 41. Liquid may be withdrawn from the zone 55 through conduit 59 provided with a control valve 60. Vapors withdrawn from the scrubbing zone 57 are conducted by conduit 61 to the liquid receiving zone 43 of the vaporizer-scrubber 41, the vapors withdrawn from the scrubbing zone 44 of the vaporizer-scrubber 41 are conducted through conduit 20 directly into the high pressure section 16 of the fractionating column.

The liquefied portion of the feed mixture is substantially completely vaporized in the vaporizer-scrubbers 41 and 53 to concentrate substantially entirely the total high boiling point impurities of the feed mixture entering conduit 10 in a small body of liquid in zone 55 that may be discharged from the cycle through conduit 59. The heat of vaporization for the vaporizer-scrubber 53 is provided by a relatively warm fluid passed through the boiling coil 56, while the heat of vaporization for the vaporizer-scrubber 41 is obtained upon liquefaction of the vapor phase portion of the feed mixture in boiling coil 46 and by a relatively warm fluid flowing through a boiling coil 62 located in the liquid receiving zone 43. Streams of product gas may be passed through boiling coils 56 and 62, or the heat of vaporization may be provided by cooling a fluid of a system relating to the fractionating operation. The latter arrangement is shown in FIGURE 1 wherein the fractionating cycle is combined with a cycle for liquefying a stream of nitrogen gas, the nitrogen stream being passed in heat exchange effecting relation with a cooled fluid of the fractionating column, such as through a boiling coil 63 located in the pool of crude oxygen 21 in the base of the high pressure section, and the refrigeration required to effect liquefaction of nitrogen stream being obtained by expanding an additional quantity of air in the expansion engine 31. Such an arrangement is disclosed and claimed in a co-pending application of J. V. Fetterman, Serial No. 636,108, filed January 24, 1957, for "Low Temperature Process." As shown in FIGURE 1, the stream of nitrogen to be liquefied is passed through the boiling coils 56 and 62 to provide the heat of vaporization required to effect the concentration of the high boiling point impurities in a small body of liquid and the arrangement is such that adequate operation of the purifying system is obtained in the presence of variations in the refrigeration requirements that may be occasioned by changes in

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the quantity of the nitrogen stream. As shown, a stream of gaseous nitrogen is fed to boiling coil 56 by conduit 64 and is cooled upon vaporizing liquid collecting in the zone 55 of the vaporized-scrubber 53. The cooled nitrogen stream is then conducted by conduit 65 for heat exchange effecting relation with the air feed in conduit 33 prior to its discharge into the phase separator 36. This heat interchange slightly warms the air feed to insure production of adequate vapor and may be accomplished in a single heat exchange zone located upstream and downstream of the expansion valve 34 or in serially connected heat exchange devices 66 and 67 as shown. The further cooled nitrogen stream is then conducted by conduit 68 through the boiling coil 62 and from the latter boiling coil by way of conduit 69 to the boiling coil 63 located in a high pressure section 16. The nitrogen stream is withdrawn through conduit 70.

In operation of the embodiment of the invention shown in FIGURE 1 of the drawings, atmospheric air, free of moisture and carbon dioxide and compressed to about 600 p.s.i.a. is introduced into the cycle through conduit 10 and is cooled upon flowing through pass 11 of the heat exchange device 12 in countercurrent heat exchange relation with oxygen and nitrogen products. About 75% of the air feed is withdrawn from the pass 11 through conduit 30 and expanded with work in expansion engine 31 to about 100 p.s.i.a. and thereby cooled to a temperature of about -270° F. The remaining 25% of the air feed is cooled to about -267° F. upon flowing through the heat exchange device 12 and is expanded in valve 34 to about 150 p.s.i.a. and further cooled to about -269° F. and then introduced into the phase separator 36. Prior to discharge into the phase separator the air feed is slightly warmed to about -267° F., upon heat exchange effecting relation with the nitrogen stream, to effect liquefaction of no more than about three-fifths of the air and thus provide about 10% of the total air feed in vapor phase from the separator 36. As discussed above, the vapor phase portion of the air from the separator 36 is substantially free of high boiling point impurities while substantially entirely the total high boiling point impurities of the air entering the separator is concentrated in the liquid phase portion. In the case of atmospheric air containing methane and acetylene impurities, of these impurities in the air entering the separator, about 4% of the methane and less than about 3% of the acetylene will be in the vapor phase portion and about 96% of the methane and more than about 97% of the acetylene will be in the liquid phase portion. In the present example, since 25% of the total air feed is fed to the phase separator, about 1% of the total methane introduced in the cycle and less than 1% of the total acetylene introduced in the cycle will be in the vapor phase portion.

The liquid phase portion is withdrawn from the phase separator at about -267° F., expanded in valve 39 to about 100 p.s.i.a. and thereby cooled to about -278° F. and then introduced into the pool of liquid in receiving zone 43 of the vaporizer-scrubber 41, the liquid in the zone 43 being at a temperature of about -275° F. The substantially impurity free vapor phase portion from the separator 36 is fed to the boiling coil 46 at 150 p.s.i.a. and about -267° F. and is cooled therein to about -270° F. and liquefied. The liquefied vapor phase portion is expanded in valve 48 to about 100 p.s.i.a. and further cooled to about -279° F. and introduced into the upper end of the vaporizer-scrubber 41 as wash liquid substantially completely free of high boiling point impurities.

The effluent from the expansion engine 31 is fed through conduit 42 into the zone 43 of the vaporizer-scrubber 41 and is scrubbed by the liquid therein materially removing high boiling point impurities therefrom. Vapor flowing upwardly in the vaporized-scrubber 41 into the scrubbing zone 44, which may be considered as comprising vapors resulting from substantially complete vaporization of the liquid portion of the air feed and

effluent of the expansion engine 31, are passed in intimate contact with impurity free wash liquid flowing over the plates 45 and leave the vaporizer-scrubber 41 free of high boiling point impurities except for a minute quantity comprising a small percentage of the high boiling point impurity in the wash liquid. The pure vapor leaves the vaporizer-scrubber 41 at 100 p.s.i.a. and -275° F. and is fed by conduit 20 to the high pressure section of the fractionating column 15. A part of the liquid portion is vaporized in the vaporizer-scrubber 41 while the remainder, about 10% of the total air feed, is vaporized in the vaporizer-scrubber 53 operating at a temperature of about -275° F. Vapor from the vaporizer-scrubber 53 is fed through conduit 61 into the vaporizer-scrubber 41 and substantially entirely the total high boiling point impurity content of the air feed entering the cycle through conduit 10 is concentrated in the liquid collecting in the zone 55 of the vaporizer-scrubber 53. The impurities may be withdrawn from the cycle through conduit 59. With this arrangement, the total air feed, less the small portion of the air feed that may be periodically removed from the vaporizer-scrubber 53, is fed to the column substantially completely free of high boiling point impurities.

The amount of liquid drained from the vaporizer scrubber 53 and removed from the cycle depends upon the concentrations of impurities in the air feed which may vary depending upon characteristics of the surrounding atmosphere. In any event, the quantity of impurities entering the fractionating column may be determined upon analysis of the liquid collecting in the base of the vaporizer-scrubber 53. For any impurity found to be present in the liquid removed from the vaporizer-scrubber 53, it is known that the quantity of such impurity has a definite relationship with the quantity of the same impurity entering the fractionating column. For example, the quantity of methane in the liquid removed from the vaporizer-scrubber will comprise about 99% of the total methane entering the cycle and the quantity of acetylene will be more than 99% of the total acetylene. Thus, the quantity of methane and acetylene entering the fractionating column may be accurately determined. Thus, the accumulation of impurities in the fractionating column are known and the necessary precautions may be taken at the proper time to insure safe operations.

The nitrogen stream enters the cycle through conduit 64 at about 1020 p.s.i.a. and -208° F. and is cooled to about -244° F. upon flowing through the boiling coil of the vaporizer-scrubber 53 and further cooled to about -254° F. in heat exchange with the air feed upstream of the phase separator 36. The nitrogen stream is cooled in the boiling coil of the vaporizer-scrubber 41 to about -256° F. and leaves the boiling coil 63 at about -265° F. The rate of flow of the nitrogen stream is about 505 moles per hour and the air enters the cycle at about 450 moles per hour with about 112 moles per hour being fed to the phase separator 36.

As described in the above-mentioned copending application of J. V. Fetterman, the refrigeration load for effecting liquefaction of a nitrogen stream is obtained by expanding a quantity of air in the expansion engine 31 greater than that which would ordinarily be necessary to maintain operation of the fractionating cycle. Under certain conditions a varying quantity of nitrogen may be passed through the conduit 64 resulting in a variation in the quantity of air passed through the expansion engine 31. Variation in the quantity of air passed to the expansion engine 31 may cause an excessive accumulation of liquid in the vaporizer-scrubber 41. Proper liquid level may be maintained in the vaporizer-scrubber 41 by feeding excess liquefied pure vapor portion directly into the high pressure column by way of control valve 49 and expansion valve 51.

The embodiment of the invention shown in FIGURE

2 of the drawings illustrates application of the present invention to a fractionating cycle in which the feed to the column is in liquid and vapor phases. This embodiment of the invention also illustrates the manner in which the incoming air feed may be utilized to effect vaporization of the liquid portion of the air feed. As shown, the portion of the air feed emerging from the cold end of heat exchange device 12 is conducted by the conduit 33 to the boiling coil 56 of the vaporizer-scrubber 53 where the air feed is cooled upon vaporizing liquid collecting in the zone 55 of the vaporizer-scrubber. The cooled air feed is expanded in valve 100 to an intermediate pressure above the pressure existing in the high pressure section 16 of the column and is then introduced into the phase separator 36. The portion of the air feed in liquid phase containing substantially entirely the total high boiling point impurity content of the air fed to the separator is expanded in valve 39 to the pressure existing in the high pressure section 16 and introduced by way of the conduit 40 into the base of the vaporizer-scrubber 41, together with the effluent from the expansion engine 31. The pure vapor from the phase separator 36 is liquefied upon flowing through boiling coil 46 and a portion of the liquefied pure vapor is expanded in valve 48 and introduced into the upper end of the vaporizer-scrubber 41 as washed liquid while the remaining portion is conducted through conduit 101 and expansion valve 102 to the high pressure section 16 of the fractionating column. If desired, a portion of the air feed in conduit 33 may be fed directly from the heat exchange device 12 to the vaporizer-scrubber 41 through conduit 103 provided with a control valve 104, depending upon the liquid feed requirements of the column. This arrangement also may be utilized for controlling the quantity of vapor obtained from the separator 36.

In operation of the system shown in FIGURE 2, the valve 32 is adjusted to feed about 25% of the total air feed to the expansion engine 31 with the remainder flowing through the heat exchange device 12 to conduit 33. Downstream of the expansion valve 100 the air is at about 150 p.s.i.a. and at a temperature such that the vapor phase portion substantially free of high boiling point impurities withdrawn from the separator 36 comprises about 35% of the total while the liquid phase portion containing substantially entirely the total impurities in 75% of the air feed, comprises 40% of the total feed. The remaining 25% of the air feed expanded to about 100 p.s.i.a. in the expansion engine 31 is fed directly to the vaporizer-scrubber 41 as also is the liquid phase portion after expansion in valve 39 to about 100 p.s.i.a. The total vapor phase portion from the separator 36 is liquefied in boiling coil 46 with one portion consisting of about 10% of the total air feed being expanded in valve 48 to about 100 p.s.i.a. and used as scrub liquid in the vaporizer-scrubber 41, while the remaining portion consisting of about 25% of the total air feed is passed through conduit 101, expanded in valve 102 and introduced into the high pressure section. The remaining portion of the air feed consisting of about 25% of the total feed, less any liquid that may be withdrawn from the vaporizer-scrubber 53, is withdrawn in vapor phase, substantially free of high boiling point impurities, from the vaporizer-scrubber 41 and introduced into the fractionating column through conduit 20. The percentage of liquid in the feed to the column may be controlled by passing air through conduit 103 directly into the vaporizer-scrubber 41 or by varying the quantity of air passed to the expansion engine 31. The temperatures of the air streams at various points throughout the system may generally correspond to the temperatures set forth in the example given for the embodiment shown in FIGURE 1. The liquefied vapor phase portion fed to the column through conduit 101 would be at about -279° F. and the temperature of the air discharged into the phase separator would be established to provide vapor

and liquid phase portion of the percentages mentioned above.

In the embodiment of the invention shown in FIGURE 3 of the drawings a portion of the air feed is liquefied and the remaining part of the air feed in vapor phase is scrubbed by the liquid portion in a scrubber-separator 125. The portion of the air feed passing through the heat exchange device 12 is conducted by conduit 33 through boiling coil 56 of the vaporizer-scrubber 53 wherein it is further cooled and is then expanded in valve 126 to an intermediate pressure above the pressure existing in the high pressure section 16 of the column such that a portion of the air is liquefied. The effluent from the expansion valve is introduced into the base of the scrubber-separator 125, so that the vapor portion passes through the body of liquid 127 retained therein. The remaining portion of the air feed is passed through conduit 30 to the expansion engine 31 and the effluent of the latter is fed to the scrubber-separator 125 into the body of liquid 127. Vapor substantially free of high boiling point impurities is withdrawn from the scrubber-separator through conduit 128 and is conducted thereby to boiling coil 46 of the vaporizer-scrubber 41 wherein the vapor is liquefied. A portion of the liquefied vapor is expanded in valve 48 to the pressure existing in the high pressure section 16 and introduced into the vaporizer-scrubber 41 as wash liquid, while the remaining portion is fed through conduit 129, expanded in valve 130 to the pressure existing in the high pressure section 16 and introduced therein as feed. The remaining portion of the air feed, comprising the liquid phase containing substantially the total high boiling point impurities of the feed mixture, is withdrawn from the scrubber-separator 125 through conduit 131 and following expansion in valve 132 to the pressure existing in the high pressure section 16 is introduced by way of conduit 133 into the base of the vaporizer-scrubber 41. If desired a portion of the effluent from the expansion engine 31 may be passed directly to the vaporizer-scrubber 41 through conduit 134 provided with a control valve 135.

In operation of this cycle atmospheric air free of moisture and carbon dioxide and compressed to about 600 p.s.i.a. is introduced to the cycle through conduit 10 with about 65% of the total feed passing through the expansion engine 31 and the remaining 35% being cooled to a low temperature in the heat exchange device 12. The cooled air from the heat exchange device is passed by conduit 33 to boiling coil 56 of the vaporizer-scrubber 53 where further cooling takes place, thereafter the stream is expanded in valve 126 to about 150 p.s.i.a. and introduced into the scrubber-separator 125 at a temperature to effect partial liquefaction, such as 25% of the total air feed. The air feed passed to the expansion engine 31 is expanded to about 150 p.s.i.a. and introduced to the scrubber-separator 125 where it is scrubbed, together with the vapor portion of the air from valve 126, with the liquid portion to substantially completely concentrate the high boiling point impurities in the liquid portion. Vapor comprising substantially 35% of the total feed and substantially free of impurities is passed through conduit 128, liquefied in boiling coil 46, expanded to about 100 p.s.i.a. and thereafter used as scrub liquid in the vaporizer-scrubber 41 and as liquid feed to the column. The liquid portion from the scrubber-separator including the impurities is expanded to about 100 p.s.i.a. in valve 132 and introduced into the zone 43 of the vaporizer-scrubber 41. The liquid portion is substantially completely vaporized in the vaporizer-scrubbers 41 and 53, and vapor substantially free of high boiling point impurities is passed through conduit 20 and introduced into the column as feed.

There is thus provided by the present invention novel method of and apparatus for effectively removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating oper-

ation. The methods and apparatus provided by the present invention are characterized by the novel feature of separating partly liquefied gaseous mixture to provide a vapor phase portion substantially free of high boiling point impurities and a liquid phase portion containing substantially entirely the total high boiling point impurity, the liquid phase portion being subsequently substantially completely vaporized, preferably in two stages, to concentrate the impurities in a small body of liquid that may be discarded from the cycle, and the vapor produced by vaporization of the liquid phase portion is scrubbed by liquefied gaseous mixture substantially free of high boiling point impurities before introduction into a fractionating operation, the liquefied gaseous mixture substantially free of impurities being obtained by liquefying vapor phase portion upon heat exchange effecting relation with the liquid phase portion under reduced pressure to effect at least a part of its vaporization. The system provided by the present invention may be used in connection with fractionating cycles requiring vapor or part liquid feed to the fractionating column and are adapted for use with arrangements in which a portion of the feed mixture is expanded with work to a relatively low pressure such as the pressure existing in the high pressure section of the two-stage fractionating column. Furthermore, the systems provided for effectively removing high boiling point impurities are capable of handling abnormal variations of high boiling point impurity content of gaseous mixtures and make it possible to accurately determine the exact quantity of high boiling point impurity entering the fractionating column.

Although several embodiments of the invention have been disclosed and described above, it is to be expressly understood that various changes and substitutions may be made therein without departing from the spirit of the invention as well understood by those skilled in the art. For example, the features shown in FIGURE 1 for providing the heat of vaporization and for controlling the temperature of the separated portion of the feed mixture by use of an extraneous nitrogen stream may be incorporated in the arrangements shown in FIGURES 2 and 3, while the cycle shown in FIGURE 1 may be modified by decreasing the percentage of air fed to the expansion engine for obtaining a required quantity of liquid feed for a fractionating column. Reference therefore will be had to the appended claims for a definition of the limits of the invention.

What is claimed is:

1. Method of removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation, which comprises cooling and partly liquefying gaseous mixture to be separated, transferring substantially the total impurities of the gaseous mixture to the liquid portion of the gaseous mixture and providing a vapor portion of the gaseous mixture substantially free of impurities, effecting substantially complete vaporization of the liquid portion containing the impurities to concentrate the impurities in the remainder, removing the remainder, passing vapor portion substantially free of impurities in heat exchange effecting relation with the liquid portion to liquefy the vapor portion and effect at least a part of the vaporization of the liquid portion, scrubbing vapor produced by the vaporization of the liquid portion with at least part of the liquefied vapor portion substantially free of impurities, and passing scrubbed vapor to the fractionating operation.

2. Method of removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation, which comprises cooling and partly liquefying gaseous mixture to be separated, separating the liquid portion of the cooled gaseous mixture containing substantially the total impurities of the gaseous mixture from the vapor portion thereof substantially free of impurities, vaporizing liquid portion containing the impurities by heat exchange with the vapor

portion to liquefy the vapor portion, scrubbing vapor produced by the vaporization of the liquid portion with a part of the liquefied vapor portion, and passing scrubbed vapor and another part of the liquefied vapor portion to the fractionating operation.

3. Method of removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation, which comprises cooling and partly liquefying gaseous mixture to be separated, separating under pressure the liquid portion of the cooled gaseous mixture containing substantially the total impurities in the gaseous mixture from the vapor portion thereof substantially entirely free of impurities, effecting substantially complete vaporization of the liquid portion containing the impurities while under reduced pressure to concentrate the impurities in the remainder, removing the remainder, liquefying vapor portion substantially free of impurities by heating exchange with liquid portion under reduced pressure, scrubbing vapor produced by the vaporization of the liquid portion with at least part of the liquefied vapor portion under reduced pressure, and feeding scrubbed vapor to the fractionating operation.

4. Method of removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation, which comprises cooling and partly liquefying gaseous mixture to be separated, scrubbing vapor portion of the gaseous mixture containing high boiling point impurities with the liquid portion of the gaseous mixture to concentrate substantially the total impurities in the liquid portion and separating a vapor portion substantially free of impurities, effecting substantially complete vaporization of the liquid portion containing the impurities to concentrate impurities in the remainder, withdrawing the remainder, passing vapor portion substantially free of impurities in heat exchange effecting relation with the liquid portion to liquefy vapor portion substantially free of impurities, scrubbing vapor produced by vaporization of the liquid portion with at least part of the liquefied vapor portion substantially free of impurities and passing vapor from the last-named scrubbing step to the fractionating operation.

5. Method of removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation, which comprises cooling and partly liquefying one portion of the gaseous mixture to be separated, separating the one portion of the gaseous mixture into a vapor portion substantially free of impurities and a liquid portion containing substantially the total impurities of the one portion of the gaseous mixture, scrubbing a second portion of the gaseous mixture with liquefied gaseous mixture to concentrate the impurities of the second portion of the gaseous mixture in the liquid portion, effecting substantially complete vaporization of the liquid portion to concentrate the impurities in the remainder, removing the remainder, liquefying vapor portion substantially free of impurities, scrubbing vapor produced by vaporization of the liquid portion with liquefied vapor portion and passing scrubbed vapor to the fractionating operation.

6. The method of removing high boiling point impurities from a gaseous mixture prior to separation in a low temperature fractionating operation as defined in claim 5, in which the scrubbing of the second portion of the gaseous mixture and vaporization of the liquid portion containing the impurities takes place in a common zone and in which liquefied vapor portion substantially free of impurities scrubs vapor produced in the zone upon vaporization of the liquid portion of the gaseous mixture in the zone.

7. Method of removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation as defined in claim 5, in which liquefaction of the vapor portion substan-

tially free of impurities is obtained by passing the vapor portion substantially free of impurities in heat exchange effecting relation with the liquid portion.

8. Method of removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation as defined in claim 7, in which a portion of the liquefied vapor portion substantially free of impurities is passed to the fractionating operation.

9. Method of removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation, which comprises cooling and partly liquefying gaseous mixture to be separated, transferring substantially the total impurities of the gaseous mixture to the liquid portion of the gaseous mixture and providing a vapor portion substantially free of impurities, effecting substantially complete vaporization of the liquid portion containing the impurities in two stages of vaporization connected in series to concentrate the impurities in the remainder, removing the remainder, liquefying vapor portion substantially free of impurities, scrubbing vapor produced by vaporization of the liquid portion with liquefied vapor portion, and passing scrubbed vapor to the fractionating operation.

10. Method of removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation as defined in claim 9, in which the liquid portion is partially vaporized in a first stage of vaporization and unvaporized liquid is fed to a second stage of vaporization wherein the vaporization is substantially completed and from which the remaining unvaporized liquid is withdrawn.

11. Method of removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation as defined in claim 9, in which vapor portion substantially free of impurities is passed in heat exchange effecting relation with liquid portion in the first vaporization zone to provide heat of vaporization and in which gaseous mixture is passed in heat exchange effecting relation with liquid in the second vaporization zone to provide heat of vaporization.

12. Method of removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation as defined in claim 9, in which a fluid stream is passed in heat exchange effecting relation with liquid in the vaporizing zones to cool the fluid stream and effect vaporization of liquid in the zones.

13. Method of removing high boiling point impurities from a gaseous mixture prior to separation by a low temperature fractionating operation as defined in claim 12, in which the fluid stream is passed in heat exchange effecting relation with the partly liquefied gaseous mixture prior to the transferring step to warm the gaseous mixture and establish the quantity of the vapor portion at said transferring step.

14. Method of removing high boiling point hydrocarbons from air prior to separation at low temperatures in a fractionating operation, which comprises compressing, cooling and partly liquefying air to be separated, separating under reduced pressure the liquid portion of the cooled air containing substantially the total hydrocarbon impurities from the vapor portion substantially free of hydrocarbon impurities, effecting substantially complete vaporization of the liquid portion containing the impurities while under further reduced pressure to concentrate the impurities in the remainder, removing the remainder, liquefying the vapor portion under reduced pressure in heat exchange effecting relation with the liquid portion under further reduced pressure, scrubbing vapor produced by vaporization of the liquid portion with at least a part of the liquefied vapor portion under further reduced pressure, and passing scrubbed vapor under further reduced pressure into the fractionating operation.

15. Method of removing high boiling point hydrocar-

bons from air prior to separation at low temperatures in a fractionating operation, which comprises compressing, cooling and partly liquefying air to be separated, separating under reduced pressure the liquid portion of the cooled air containing substantially the total hydrocarbon impurities from the vapor portion substantially free of hydrocarbon impurities, scrubbing air under the further reduced pressure with liquid portion of the air, effecting substantially complete vaporization of the liquid portion containing the impurities while under further reduced pressure to concentrate the impurities in the remainder, removing the remainder, liquefying the vapor portion under reduced pressure in heat exchange effecting relation with the liquid portion under further reduced pressure, scrubbing vapor produced by vaporization of the liquid portion and scrubbed air under the further reduced pressure with at least a part of the liquefied vapor portion under the further reduced pressure, and passing vapor from the last-named scrubbing step to the fractionating operation.

16. Method of removing high boiling point impurity from gaseous mixture prior to separation in a fractionating zone under low temperature, which comprises cooling and partly liquefying gaseous mixture to be separated, passing the liquid portion of the gaseous mixture to a first zone and transferring substantially the total high boiling point impurity of the gaseous mixture to the liquid portion in the first zone, passing a relatively warm fluid in heat exchange relation with liquid in the first zone to partly vaporize liquid in the first zone and concentrate high boiling impurity in unvaporized liquid in the first zone, withdrawing unvaporized liquid from the first zone and passing withdrawn unvaporized liquid to a second zone, passing a relatively warm fluid in heat exchange relation with liquid in the second zone to effect substantially complete vaporization of liquid in the second zone and concentrate high boiling point impurity in the remaining liquid, withdrawing the remaining liquid from the second zone and discarding such remaining liquid, scrubbing vapor produced upon vaporization of liquid in the first zone and vapor produced upon vaporization of liquid in

the second zone with liquid free of high boiling impurity, and feeding scrubbed vapor to the fractionating zone.

17. Apparatus for removing high boiling point impurity from a gaseous mixture prior to separation at low temperature in a fractionating column, comprising means for cooling and partly liquefying compressed gaseous mixture to be separated, a phase separator for receiving partly liquefied gaseous mixture, a vaporizer-scrubber having a liquid receiving zone and a scrubbing zone, means for expanding liquid portion of the gaseous mixture withdrawn from the phase separator to a lower pressure and for introducing the expanded liquid into the liquid receiving zone of the vaporizer-scrubber, means for passing vapor portion of the gaseous mixture withdrawn from the phase separator in heat exchange with the liquid in the liquid receiving zone of the vaporizer-scrubber to partly vaporize liquid in the vaporizer-scrubber and provide liquefied vapor portion, vaporizer means, means for withdrawing unvaporized liquid from the vaporizer-scrubber and introducing such unvaporized liquid into the vaporizer means, means for passing relatively warm fluid in heat exchange with liquid in the vaporizer means to effect substantially complete vaporization of liquid in the vaporizer means, means for withdrawing unvaporized liquid from the vaporizer means, means for feeding vapor withdrawn from the vaporizer means to the vaporizer-scrubber, means for expanding the liquefied vapor portion to the lower pressure and introducing at least a part of the expanded liquid into the scrubbing zone of the vaporizer-scrubber, and means for withdrawing scrubbed vapor from the vaporizer-scrubber and feeding such vapor to the fractionating column.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,065,607

November 27, 1962

Clarence J. Schilling 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 1, line 34, for "same" read -- safe --; column 3, line 20, for "of" read -- by --; column 4, line 21, for "flowing" read -- flows --.

Signed and sealed this 18th day of June 1963.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

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Commissioner of Patents