

Sept. 1, 1953

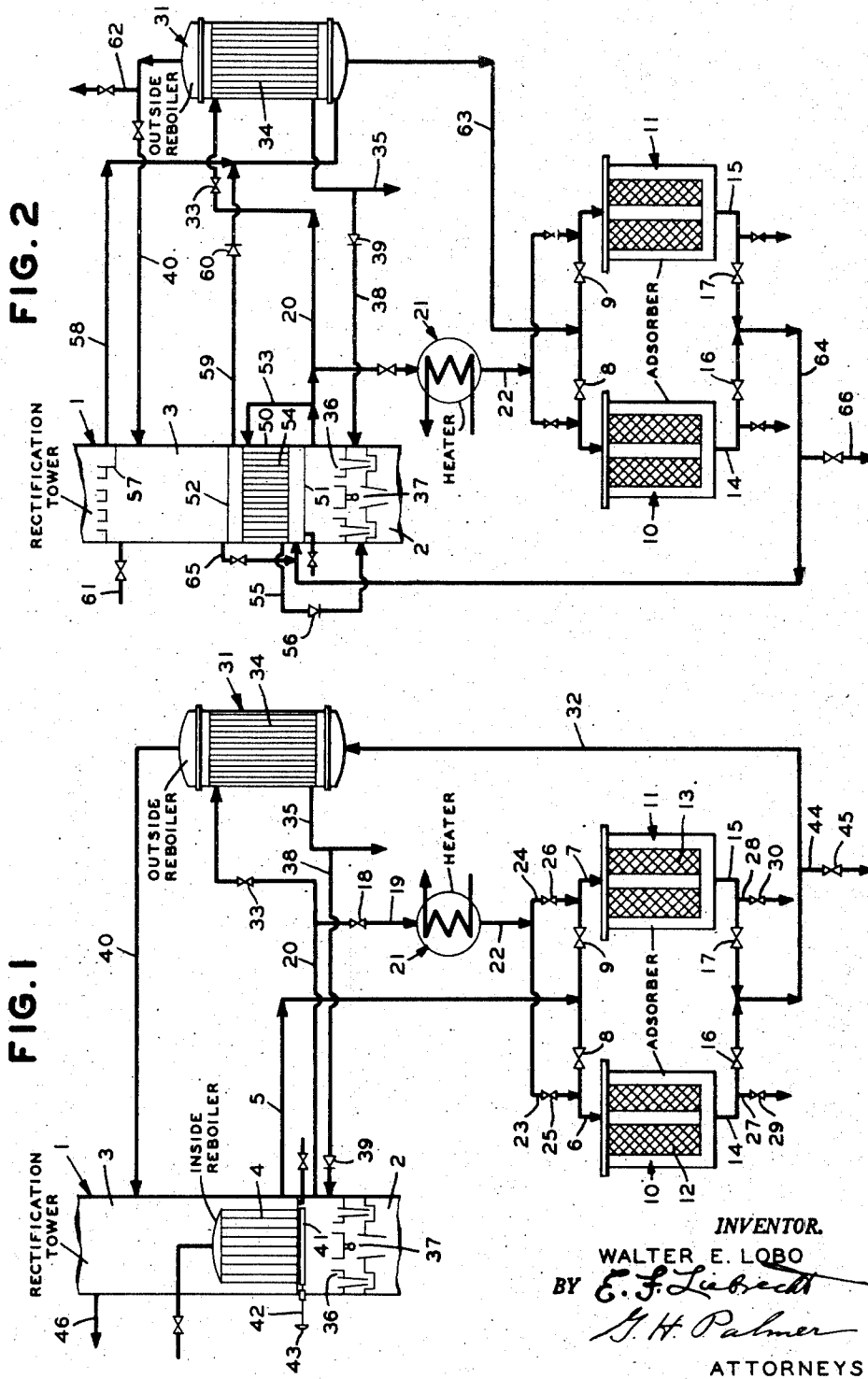
W. E. LOBO

2,650,482

METHOD OF SEPARATING GAS MIXTURES

Filed April 29, 1948

2 Sheets-Sheet 1



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FIG. 3

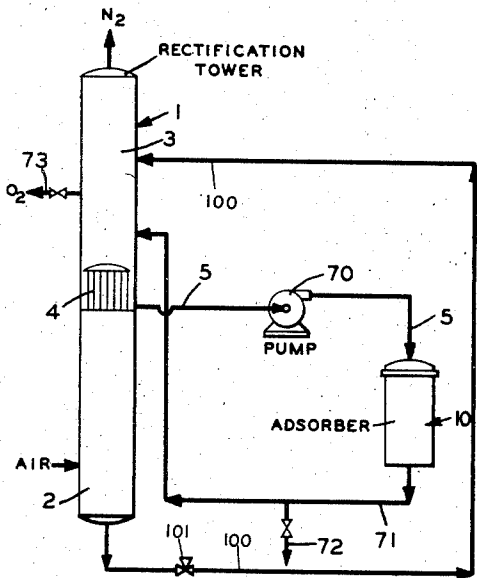


FIG. 4

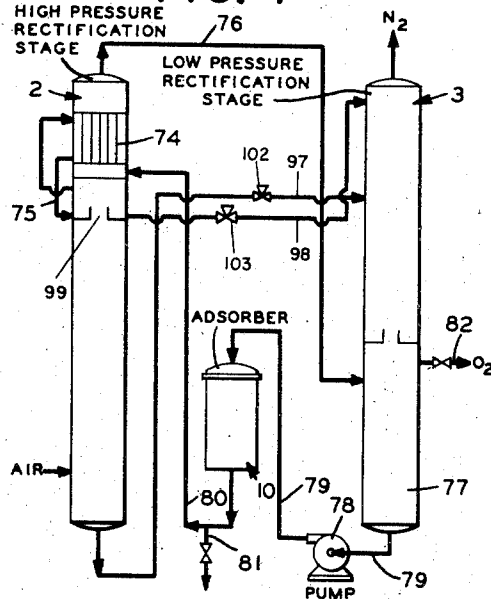


FIG. 5

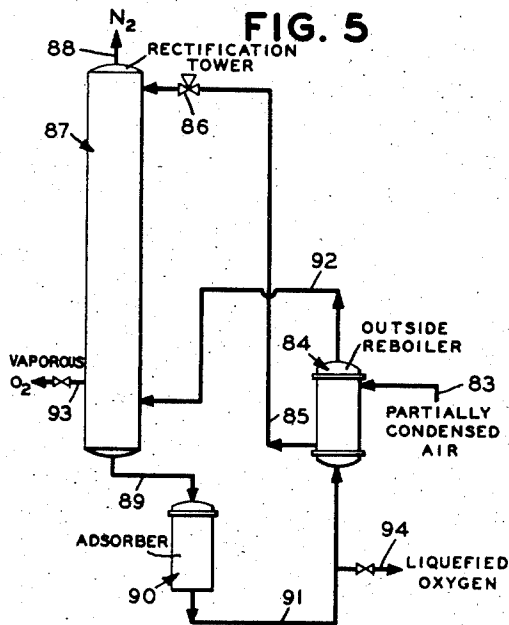
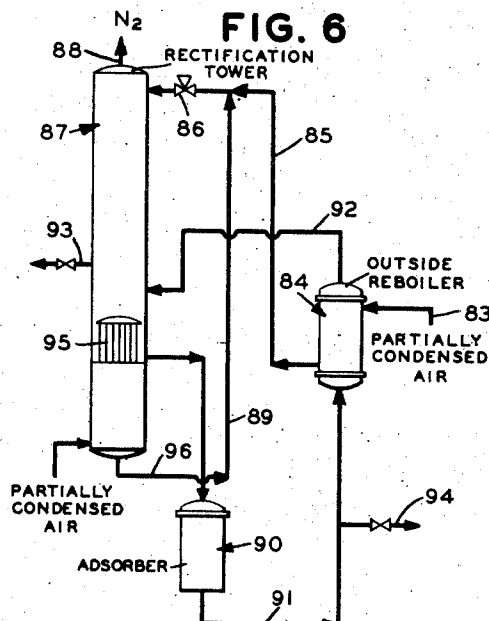


FIG. 6



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METHOD OF SEPARATING GAS MIXTURES

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10 Claims. (Cl. 62—175.5)

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This invention relates to improvements in the separation of normally gaseous mixtures, containing higher boiling components as undesirable impurities, by low temperature liquefaction and rectification. More specifically, the invention relates to the removal of a higher boiling component from a liquefied gas, such as one comprising carbon dioxide, air, oxygen, or hydrocarbons, the concentration being such that as a rule the component does not materially change the boiling point of the liquefied gas, but is otherwise objectionable because it either impairs the purity of the product or by its presence creates an explosive hazard in operating the separation process.

A specific object of this invention is to accomplish the substantially complete removal of an impurity from a liquefied gas in a rectification zone or to reduce the concentration thereof to a concentration within safe operational limits.

Another object is to remove dissolved impurity from a liquefied gas by the continuous and forced recirculation of the liquefied gas through a body of solid adsorbent material.

A further object is to remove dissolved normally gaseous impurity from a liquefied gas by the continuous and forced recirculation of portions of the liquefied gas through a body of granular particles of solid adsorbent material.

A still further object is to remove dissolved normally gaseous impurity from a liquefied gas by recirculating continuously through a body of solid adsorbent material a stream of the liquefied gas maintained in positive flow conditions by a "thermal siphon" effect established and maintained by partial vaporization of the circulating liquefied gas.

It is also an object to utilize the heat derived from condensing vapors of a higher pressure rectification zone to establish and maintain a "thermal siphon" for the forced recirculation of a stream of a liquefied product of a lower pressure rectification zone through a closed circuit including a body of adsorbent material for adsorbing a dissolved impurity from the liquefied product.

Other objects will become apparent in the more detailed explanation of the invention with reference to illustrative examples concerning the removal of acetylene from the air in connection with the separation of air by the well-known procedure of low temperature rectification.

The separation of atmospheric air into oxygen-rich and nitrogen-rich products by liquefaction and rectification at low subatmospheric temperatures requires the use of relatively large quantities of air. Consequently, even insignificant amounts of impurities in the feed air readily can become greatly magnified if not removed continuously. During the forecooling step of the

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process some higher boiling gaseous impurities condense as liquids and solids on the cooling surfaces, and in time accumulate in such quantities as to restrict the gas flows and upset the plant operation. By employing the principle of reversing heat exchange to perform the main cooling step of the process, either by means of regenerators or exchangers, water and carbon dioxide in particular may be so effectively removed that long time plant operating schedules are possible. Hydrocarbons, however, are seldom present in the feed air in concentrations great enough to cause condensation and thereby their removal in the main forecooling step. Yet these hydrocarbons must be removed from the plant by some means, as they not only interfere with the flows but also introduce a hazard. By the nature of the process, traces of hydrocarbons in the feed air finally accumulate in the reservoir of oxygen-rich liquid at the bottom of the main rectification stage. With a sufficient concentration of hydrocarbons in the oxygen-rich liquid, the plant is liable to damaging explosions in the event the reaction is detonated by some priming agent. It is known that acetylene is present in atmospheric air and that it accumulates in the oxygen-rich liquid as a solid explosively sensitive to shock, electro static charges, or even sudden temperature changes, particularly if ozone also is present in the liquid. While the acetylene concentrations in air are usually small, the saturation concentrations in the oxygen-rich liquid are also small. For example, solid acetylene may be precipitated when it reaches the low concentration of three parts per million by volume in the oxygen-rich liquid.

Beds of adsorptive materials have been employed at the cold outlet of the forecooling step, on the inlet line to the expander, and on the oxygen-enriched liquid air line of a conventional two stage rectifying column, these beds being designed to take advantage of the high adsorptivity of solid adsorbents at low temperatures and under pressure. The beds usually are relatively large in size, require large amounts of refrigeration for cooling preliminary to being placed in service initially and after each regeneration period, and suffer the additional disadvantage in that they are subject to by-passing either through faulty operation or through defects in construction. These devices situated as they are in the plant processing arrangement, are not capable of being used to remove any impurities that may have by-passed the adsorbent in a period of faulty operation.

Hydrocarbons also have been removed from the oxygen-rich liquid by an evaporative procedure. This procedure, however, concentrates the explosive impurities in a small stream of liquid oxygen that has to be wasted at the expense of

the plant's refrigeration and, therefore, lowers the plant's power economy. This evaporative method is hazardous because there is no certainty that all of the hydrocarbons are contained in the waste liquid stream since some, for example, may be entrained in the rising vapors of evaporation and deposited in a location where they are particularly liable to explode. Also, great care must be exercised to avoid explosions in the disposal line.

The present invention will be illustrated by its application to the removal of acetylene from the "so-called" low pressure rectification stage of an air separation plant producing an oxygen-rich product. According to this application of the invention, the oxygen-rich liquid at the base of the low pressure stage is recirculated over adsorptive solids which remove the acetylene at such a rate that, over the operating cycle of the adsorber, precipitation of the dangerous solid phase of acetylene at all points of the circuit is avoided. This procedure eliminates acetylene at its point of final accumulation in the air separation plant. It accomplishes this removal in a safe procedure without allowing the acetylene to reach the dangerous or solid state in the plant or in the remaining equipment. Because of the recirculation procedure, imperfections in the adsorption step are less serious since traces of acetylene that escape adsorption on their first pass through the adsorptive bed are eventually adsorbed in subsequent passes through the bed. Acetylene escaping adsorption during "start-up periods" is adsorbed later when the adsorptive bed is functioning effectively.

For a more complete understanding of the process of the invention, reference is had to the following detailed description taken in connection with the accompanying drawings, in which:

Figure 1 diagrammatically represents a portion of a two-stage rectification tower and a closed recirculation system for passing liquefied gas through a body of adsorbent in accordance with a preferred modification.

Figure 2 diagrammatically shows an alternative arrangement of apparatus for recirculating liquefied gas through a body of adsorbent material.

Figure 3 and 4 diagrammatically illustrate a further alternative arrangement for recirculating continuously through a body of adsorbent material a stream of liquefied gas maintained in positive flow conditions.

Figures 5 and 6 show diagrammatically the application of the process of the invention according to the preferred modification in connection with a single stage rectification tower.

In the preferred modification, as applied to a two-stage rectification operation, the method of the invention utilizes a closed recirculation system wherein the liquefied oxygen-rich liquid accumulating in the bottom of the low pressure, or main, rectification stage is passed continuously through a body of adsorbent material. A portion of this liquid is reboiled to provide vaporized product and the vapor upflow for rectification. Circulation of liquid through the adsorbent preferably is induced by a "thermal flow" effect established by the "siphon action" set up by a reboiler which may be within or external to the rectifying column and may provide either part or all of the reboiling required. Heat for reboiling is obtained by heat exchange between vaporizing oxygen-rich liquid and condensing vapors of nitrogen from the top of the preliminary, or high pressure, rectification stage.

According to one processing arrangement incorporating the preferred modification wherein recirculation is effected by an external reboiler, the reboiling step is performed downstream from the adsorption step and in this event the vaporized and unvaporized portions of acetylene-denuded liquid preferably are returned through a common conduit to the vapor space below the bottom tray of the main rectification stage. After vapor-liquid separation the unvaporized portion from the external reboiler is commingled with the main body of oxygen-rich liquid in the rectifying tower. The vaporized portions are partially withdrawn as product material and the remainder is permitted to pass upwardly through the rectification stage. According to an alternative processing arrangement, the reboiling step to establish liquid circulation is performed prior to the adsorption step in which case an internal reboiler preferably promotes positive fluid circulation and the partial vaporization of the oxygen-rich liquid in the external reboiler is carried out primarily to produce only the residual vaporization required. The primary requisite of the method is to adjust the rate of flow of liquid through the adsorption step to keep the acetylene concentration in the liquid returning to the rectification stage sufficiently low so that when this liquid again is commingled with the main body of oxygen-rich liquid the overall acetylene concentration therein is maintained below the concentration at which crystals of acetylene precipitate for the calculated amount of vaporization in the rectification column. This rate of flow therefore is a variable condition dependent upon the efficiency of acetylene adsorption per pass in conjunction with the acetylene content in the liquid downflow of the main rectification stage.

Referring now to Figure 1, rectification tower 1, which is constructed in the conventional manner for rectifying air, is separated into two compartments or stages denoted by the numerals 2 and 3. For the purpose of this description only the top portion of stage 2 and the bottom portion of stage 3 are shown, as these portions only are necessary to the description. Stage 2 represents the first, or high pressure, rectification stage wherein the precooled compressed air is rectified primarily into liquefied oxygen-enriched air by removing overhead a part of its nitrogen content. The nitrogen thus separated is condensed and both products of the primary rectification, preferably also subcooled, are then expanded into the second, or main, rectification stage 3, together with another portion of cold expanded air, for separation into nitrogen-rich or oxygen-rich final products. This latter rectification is performed under a lower pressure than the pressure of the first rectification stage.

The liquid downflow of the second rectification accumulates in a pool at the bottom of stage 3 around the outside of the tubes of the reboiler apparatus 4. Although the apparatus for reboiler 4 is shown in the figure as being a capped bundle of tubes located in the bottom of stage 3 but having the inside of each tube opening into the vapor space at the top of stage 2, the design of this reboiler is not to be limited to this specific arrangement. For example, a reboiler designed somewhat similar to reboiler 50 of Figure 2 having suitable liquid and vapor connecting lines to stages 2 and 3 would be just as satisfactory for carrying out the function of reboiler 4. In any event the liquid at the bottom of rectification stage 3 is reboiled to provide the vapors

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for rectification and vaporous product to be withdrawn from the system. To prevent build-up of liquid around the reboiler the liquid reevaporized necessarily must be equivalent to the liquid passing down the rectification column into the pool. Since acetylene has a negligible vapor pressure under the conditions at which this vaporization takes place, only a negligible quantity of this material which enters the pool is removed in the evolved vapors. The highest acetylene concentration in the air separation system exists at this point since vaporization, particularly when producing a vaporous product, is the primary means for removing material from the pool.

Figure 1 illustrates the removal of acetylene according to the invention in an air separation process in which approximately 30,750 pounds per hour of oxygen-rich liquid enters the liquid pool surrounding reboiler 4 from the bottom tray of rectification stage 3 of which 11,165 pounds per hour is subsequently removed through line 46 as vaporous product. Stage 3 of the rectification operates under a pressure of 25 pounds per square inch absolute and this necessitates a reboiling temperature in the liquid pool of -290°F . The heat required to boil vapors from the pool, equivalent to the quantity of liquid entering it, is derived from the condensation of 21,449 pounds per hour of nitrogen vapors reaching the top of the high pressure rectification stage 2. This latter stage operates under a pressure of 105 pounds per square inch absolute so that the nitrogen vapors entering into heat exchange relation with the oxygen-rich liquid are approximately at -280°F . Inasmuch as the atmospheric air charged to the separation process may contain on the average about one part of acetylene per million parts of air on a gaseous volume basis, hereinafter referred to simply as a certain number of parts per million of acetylene, the down-flowing oxygen-rich liquid continuously is bringing into the liquid pool around reboiler 4, about two parts per million of acetylene. This acetylene must be removed with enough efficiency to keep the concentration of acetylene in the liquid pool around reboiler 4 below three parts per million so that the rectification can be carried out within safe operational limits.

The oxygen-rich liquid is circulated continuously through a body of adsorbent material to remove its acetylene constituent. In the present illustrative process, a maximum of 55% of the liquid surrounding the tubes of reboiler 4 is vaporized thereat so that the acetylene concentration in the remaining liquid cannot do more than double its value. The process must be operated, however, in a manner to preclude precipitation of solid particles of acetylene even in the event that the acetylene concentration in the liquid downflow is doubled. This is done by continuous recirculation of the oxygen-rich liquid through an adsorbent which eliminates any disadvantage arising from lowered adsorption efficiency, a deficiency attendant with "once through" procedure, and thus assures greater certainty of removing enough acetylene to maintain the required low concentration thereof in the reboiler liquid.

The adsorptive capability of the flow arrangement of Figure 1, therefore, is adaptable to variations in the concentration of acetylene in the atmospheric air being charged to the separation system. The present process for describing Figure 1 is based upon an exemplary feed air mixture initially containing an average of acetylene

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concentration of one part per million. With a feed of this character and with a design in which the adsorption capacity of a bed of adsorbent is of such proportions as to be capable of effectively removing substantially all of the acetylene from the oxygen-rich liquid contacting it in a single pass, the adsorption system can readily maintain a maximum tolerable acetylene concentration of two parts per million in the liquid surrounding the tubes of reboiler 4. On the basis of completely removing the acetylene from the oxygen-rich liquid in one pass through the adsorber, a circulation rate equal to the total rate of vaporizing the oxygen-rich liquid is sufficient to prevent the accumulation of acetylene. However, as it is always advisable in commercial installations to provide for certain inefficiencies of adsorption such as may be encountered when a bed of adsorptive material has been on stream for some time and is approaching need for regeneration, this description is presented from the point of view that the adsorber effectively operates at 50% efficiency. Thus oxygen-rich liquid which contacts the adsorber with two parts per million of acetylene and leaves this contact with one part per million necessarily must have a circulation rate approximately double the minimum circulation rate of complete adsorption, or equal to the feed rate in mols per hour of the atmospheric air to the process. A circulatory flow through the adsorption system approximating at least a circulation rate equal to the feed air rate to the separation process eliminates the phenomenon of total vaporization heretofore employed in the bottom of rectification stage 3 and thus eliminates the certainty of acetylene precipitation at this point. Furthermore, even if the feed air were to have an acetylene concentration of two parts per million increasing the circulation rate of liquid through the adsorber permits the adsorbent to reduce the acetylene concentration in the pool of liquid around the tubes of reboiler 4 to below one and a half parts per million and thus definitely prevents formation of solid particles of acetylene.

Figure 1 illustrates a preferable method for circulating the oxygen-rich liquid by "thermal flow." By this method, reboiler 4 is operated to vaporize 17,000 pounds of liquid per hour. Meanwhile, 57,200 pounds per hour of liquid is withdrawn through line 5 and taken through one or the other of connecting lines 6 or 7, having valves 8 and 9 respectively, for introduction into either of the adsorbers 10 or 11. These vessels contain granular adsorbent material which preferably is silica gel. The beds may be of any suitable arrangement but conveniently the silica gel is placed in an annular space between two perforated cylindrical walls to form the bodies of adsorbent denoted by the numerals 12 and 13 respectively. The beds of adsorptive material 12 and 13 are necessarily designed to accomplish the desired degree of adsorption and in the present illustration, have a volumetric capacity of 18.7 cubic feet. This capacity is sufficient to retain approximately 748 pounds of silica gel in a mass of such density as to cause only about 0.2 pound per square inch pressure drop through the adsorber which represents a design based on twice the required circulation rate and 41% of the maximum allowable space velocity through the beds. The incoming liquid enters the inner space of beds 12 and 13 and then passes more or less horizontally therethrough into an outer space confined by the walls of adsorbers

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10 and 11. In passing through the adsorbent at the flow conditions of this operation, the oxygen-rich liquid is substantially completely denuded of its acetylene content by the time it is withdrawn from the adsorbers through either of the connecting lines 14 or 15, having valves 16 and 17 respectively. It is possible that the action by beds 12 and 13 is not effected by adsorption but by absorption or by both actions. Whenever the term "adsorption" is used herein-

after, it consequently also includes "absorption." At periodic intervals, which may conveniently be once every 24 hours, it becomes necessary to regenerate the adsorbers. This is done conveniently by closing valves 8 and 16 or 9 and 17, depending upon which of the adsorbers 10 or 11 is undergoing regeneration, opening the corresponding pair of valves for the other adsorber and opening valve 18 in line 19. When valve 18 is opened, nitrogen vapor is taken from line 20 and passed through line 19 to heater 21. At this point the temperature of the nitrogen is raised to a temperature suitable for purging acetylene from the adsorbent material. The heated nitrogen vapor is then taken from the heater through line 22 and passed by way of either of the connecting lines 23 or 24, valve 25 or 26 respectively being open, into line 6 or 7 for passage through the adsorber undergoing regeneration. The regenerating vapor commingled with vaporized acetylene leaves either adsorber 10 or 11 by way of line 14 or 15 and is purged from the system by either purge line 27 or 28, valve 29 or 30 being open for this purpose.

After undergoing contact with the silica gel in the adsorption step, the acetylene-denuded liquid is passed to the outside reboiler 31 by way of line 32. For the case in which the product is withdrawn from the rectification in the liquid phase, it may be conveniently removed from line 32 by line 44, valve 45 being opened for this purpose. In any event, it is the function of outside reboiler 31 to take acetylene-denuded liquid passing thereto in line 32 and to begin and maintain a positive circulatory flow by a "so-called" thermal siphon action created by vaporizing that portion of the liquid which must be vaporized over and above the vapors evolved by reboiler 4 so as to make the total reboiled vapors, or withdrawn liquid product and reboiled vapors, equivalent to the liquid downflow. In the present operation with a vaporized product, these vapors amount to 13,750 pounds per hour and, for supplying the necessary heat to produce these vapors, valve 33 is actuated to bring 17,351 pounds per hour of vaporous nitrogen from the top of the high pressure rectification stage through line 20 to reboiler 31 at a temperature of approximately -280° F. These warm vapors pass through the shell side of reboiler 31 on the outside of tubes 34, in countercurrent heat exchange relation with the acetylene-denuded liquid passing upwardly through the tubes, and are condensed thereby. Nitrogen condensate leaving the reboiler at a temperature of approximately -281° F. through line 35 may be combined with additional amounts withdrawn from tray 36 through line 37 if such is necessary and then passed to an upper point in rectification stage 3 in a manner not shown on the drawing. In the event it becomes necessary to employ a larger quantity of nitrogen vapors for the above heat transfer heat relationship, the excess condensate is returned to high pressure rectification stage 2 by way of line 38, having check valve 39 positioned therein to prevent backward-return of any liquid from recti-

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fication stage 2. The vaporous and unvaporized portions of the acetylene-denuded liquid leave reboiler 31 at about -290° F. through line 40 and are conducted through this line back to the low pressure rectification stage 3. Should it become necessary or desirable to change the circulation rate through the adsorption system, this is done by employing valve 33 as a control valve. For instance, the valve may be opened somewhat to divert more of the condensing nitrogen to outside reboiler 31. The resultant effect of this diversion would be to increase the vaporization rate in the reboiler thereby establishing an increase of liquid flow through the circulatory adsorption system and correspondingly decreasing the vaporizing effect of inside reboiler 4.

In the present illustration, to achieve a suitable "thermal flow" of liquid through the circulatory adsorption system, lines 5 and 32 and the connecting lines 6, 7, 14 and 15 have been designed so as to create no more than about 0.33 pound per square inch pressure drop to the inlet of reboiler 31 plus, of course, the 0.2 pound per square inch pressure drop through either of the adsorbers. The pressure drop through the outside reboiler 31 has been determined to be of the order of 0.24 pound per square inch while line 40 is constructed of suitable cross-sectional area to have a pressure drop of about 0.22 pound per square inch. The summation of pressure drops through each part of the system determines the required driving force for actuating the specified circulation rate of the oxygen-rich liquid there-through. This driving force is created by the density difference between the fluids in reboiler 31 and the bottom of rectification stage 3 as well as by the positioning of outside reboiler 31 at a level below the average level of the liquid pool surrounding the tubes of reboiler 4 while also taking into consideration the pressure head necessary for returning condensed nitrogen to the top tray of rectification stage 2.

The material from line 40 is returned to rectification stage 3 in the vapor space above the surface of the liquid around reboiler 4 and below the bottom rectifying tray to effect a separation between the liquid and vapor phases. In this illustrative procedure, 13,750 pounds per hour of vapors are derived by the heating obtained in outside reboiler 31 and these vapors, combined with the 17,000 pounds per hour of vapors derived from the heating effect of reboiler 4, provided both the 11,165 pounds per hour of oxygen-rich product, withdrawn through line 46, and 19,585 pounds per hour vaporous upflow for the rectification. Simultaneously, 43,450 pounds per hour of acetylene-free liquid likewise are derived from line 40 and this liquid once again becomes commingled with the oxygen-rich liquid surrounding the tubes of reboiler 4, and by this commingling the acetylene concentration in the liquid pool at the base of rectification stage 3 is maintained at approximately one part per million.

Alternatively, to the process flow arrangement described hereinabove, reboiler 4 may be omitted and its function included in the performance of outside reboiler 31. Reboiler 4 may be removed from operation by any means such as filling the tubes with inert gas or conveniently by blocking off the tubes thereof to the flow of nitrogen vapors, as by a movable perforated cover plate 41. This plate is retained in position by suitable brackets in a manner to permit a desired freedom of movement. The plate contains perfora-

tions comparable in location and size to the location and inside diameter of the tubes of reboiler 4. A rod 42 is attached to plate 41 and extended through the wall of the rectification column being properly bushed to prevent leakage around the rod. By means of a hand device 43 outside the column, rod 42 can be manipulated so as to change the position of plate 41 in its retaining brackets enough to entirely block the upward flow of vapors into the tubes of reboiler 4. In this event, the pool of oxygen-rich liquid at the bottom of rectification stage 3 becomes a reservoir to receive and hold both the liquid downflow of rectification and unvaporized portions of the acetylene denuded liquid from line 40. The oxygen-rich liquid for circulation through the adsorbing and vaporizing steps is then withdrawn through line 5 from this reservoir. Circulation of the oxygen-rich liquid from and to the bottom of rectification stage 3, as before, must be at such rate as necessary to maintain the acetylene concentration therein below the main concentration required for safe operation. With omission of reboiler 4 all the vapors of nitrogen passing to the top of rectification stage 2 are taken through line 20 for condensation through outside reboiler 31. The total liquid reflux for the high pressure rectification step is then returned from reboiler 31 by way of line 38.

While circulation of the oxygen-rich liquid through the circulatory adsorption system has been described as being sustained by the "thermal flow" conditions provided by the outside reboiler 31, the same flow conditions may be maintained by interchanging the functions of the inside and outside reboilers. Figure 2 diagrammatically represents a process arrangement wherein the positive flow of liquid through the adsorption system is provided by a reboiler located within rectification column 1. According to this processing method, the design of the inside reboiler is changed somewhat, for example by a heat exchanger 50 for reboiling which is positioned intermediately between rectification stages 2 and 3 but entirely separated therefrom by a bottom plate 51 and a top plate 52. All of the nitrogen vapors are now withdrawn from the top of rectification stage 2 through line 20 but part of these vapors are diverted from line 20 into line 53, introduced therethrough into the shell side of the tubes 54 of reboiler 50, and are condensed by heat exchange relation with oxygen-rich liquid passing upwardly within the tubes. The condensed nitrogen is then withdrawn from reboiler 50 and passed to the top tray 36 of rectification stage 2 by way of line 55 having check valve 56. The other part of the nitrogen vapors passing through line 20 are introduced into the shell side of the tubes 34 of outside reboiler 31. The quantity of vapors flowing through line 53, is controlled by the setting of control valve 33. Within reboiler 31 the nitrogen vapors pass downwardly in countercurrent heat exchange with oxygen-rich liquid rising through the inside of tubes 34 and are condensed thereby after which the condensate is removed through line 35 as heretofore described. Any of the nitrogen condensate needed for refluxing purposes in rectification stage 2 is taken from line 35 through line 38 to the upper tray 36. Check valve 39 prevents back-flow of liquid through line 38 in the event of pressure fluctuations in rectification stage 2.

Referring now specifically to rectification stage 3 of Figure 2, oxygen-rich liquid downflowing

from the vapor-liquid contacted in this stage, is collected on tray 57. This liquid is removed from the tray through line 58. Simultaneously, an out-flowing mixture of vapor and liquid from the top of reboiler 50 is taken through line 59, having check valve 60, and passed into line 58. The commingled streams in this line are introduced into the bottom of reboiler 31 and brought into heat exchange relation with condensing nitrogen vapors from line 20 for further vaporization. The vapors are removed from the top of reboiler 31 and returned through line 40 to the vapor space below the lower most tray of rectification stage 3. Product vapors are withdrawn from this space through the valved line 61 and the vapors not so withdrawn pass upwardly through the several rectifying trays of the stage. The product vapors alternatively may be withdrawn directly from line 40 through the valved line 62. That part of the oxygen-rich liquid not vaporized in reboiler 31 is removed from the base of the reboiler through line 63 to the adsorption stage. There, the liquid undergoes adsorption in the manner as heretofore described in connection with Figure 1 after which it is subsequently caused to flow through line 64 into the bottom section of reboiler 50 to undergo the necessary heating for promoting the positive flow through the adsorption circuit. When a liquefied product is desired, this product may be withdrawn from line 64 by valved line 66 and conditions adjusted in the operation of the liquid recirculation to permit this withdrawal. In case there is an accumulation of liquid in the bottom of rectification stage 3, such liquid may be drained from the stage through valved line 65 and added to the liquid flowing through line 64.

Figure 3 illustrates the application of the method of the invention in a rectification zone wherein all of the reboiling for the low pressure stage is effected by inside reboiler 4. In this figure only the essential parts of the apparatus that is necessary for the description has been shown as it is understood that rectification tower 1 separates air according to the conventional two stage operation for such rectification. Likewise, only one absorber vessel is shown, it being understood that this vessel may be taken off stream for regeneration and a second one used for adsorption in the manner heretofore described. The method of purifying the oxygen-rich liquid follows the procedure as described in connection with the foregoing figures. Line 100, having an expansion valve 101, connects the bottom of high pressure rectification stage 2 with an intermediate point of low pressure rectification stage 3 for the purpose of transferring liquefied oxygen-enriched air from the former to the latter-mentioned rectification stage. In the present instance, however, 57,200 pounds per hour of the oxygen-rich liquid are recirculated from rectification stage 3 through line 5 under positive flow conditions maintained by pump 70 to adsorber 10. Upon its passage through the bed of adsorbent in adsorber 10 the oxygen-rich liquid is substantially denuded of its acetylene constituent when it is passed through line 71 back to rectification stage 3. The continuous commingling of the liquid from line 71 with the body of liquid surrounding the heat exchange tubes of reboiler 4 maintains the acetylene concentration of the liquid body at approximately one part per million. The present procedure is particularly adaptable for separations producing substantially pure liquid oxygen as such product may be removed con-

veniently from line 71 by the valved line 72. A vaporous product may be recovered alternatively directly from the rectification tower through valved line 73.

While it is a convenient practice to super-impose rectification stage 3 above stage 2 in a single integral vessel, such an arrangement is not a necessary requisite for the rectification. The modification of the circulatory acetylene adsorption system illustrated by Figure 4 is particularly suitable in its application to rectification stages which perform their function in separate vessels positioned side by side. In this case positive circulation of the oxygen-rich liquid between the bottom of low pressure rectification stage 3 and reboiler 74 is maintained by a pump 78 by way of lines 79 and 80 and the intermediately disposed adsorber 10. By employing a pump to maintain positive flow conditions, the function of reboiling for stage 3 may be carried out entirely by condensing nitrogen vapors in reboiler 74 at the top of the high pressure rectification stage 2. This permits the convenient return of reflux liquid to stage 2 by gravity flow through line 75. Condensation of the nitrogen vapors outside the tubes in reboiler 74 partially vaporizes the oxygen-rich liquid passing upwardly inside the tubes after delivery thereto from the low pressure rectification stage 3. The mixture of vapors and liquid thus formed in reboiler 74 are passed through line 76 into the vapor space 77 below the bottom tray of stage 3 which space serves in the dual capacity of separator and liquid reservoir. From this reservoir the oxygen-rich liquid is pumped by pump 78 by way of line 79 through adsorber 10 and then line 80 back into the bottom section of reboiler 74. Lines 97 and 98 connect between tower 2 and tower 3 for transferring oxygen-enriched liquefied air and liquefied nitrogen respectively from the higher pressure to the low pressure rectification stage. Expansion valves 102 and 103 are positioned in lines 97 and 98 respectively to expand the material being transferred therethrough from the higher pressure of rectification stage 2 to the lower pressure of rectification stage 3. An oxygen-rich liquid product may be removed from line 80 through the valved line 81 or in the event a vaporous product is desired such product may be removed directly from the low pressure rectification stage 3 through valved line 82.

The aforescribed applications of the invention has been illustrated by Figures 1 and 2 with reference to two stage rectification for a separation. It is to be understood that the invention is equally as applicable to single stage rectification which may be more clearly understood by reference to the diagrammatic process flow arrangements illustrated in Figures 5 and 6. For example, by now referring to Figure 5, compressed and partially liquefied air is introduced by way of line 83 into reboiler 84 wherein it relinquishes its heat of condensation and is totally in the liquid phase as it flows through line 85 and is expanded through expansion valve 86 into the top of rectification tower 87 as reflux liquid. In tower 87 the liquefied air is rectified into a vaporous nitrogen-rich top product which is withdrawn from the tower through line 88 and an oxygen-rich liquid bottom product which accumulates in the base of the tower. The heat liberated in reboiler 84 by the final condensation of the partially liquefied feed air from line 83 creates a "thermal siphon" effect and by "thermal flow" causes the circulation of the oxygen-rich liquid from the base of tower 87 through

line 89, the body of adsorbent in adsorber 90 and line 91 into reboiler 84. In this vessel the liquid is partially vaporized by the heat exchange with the condensing air so that it is a mixture of acetylene-denuded vapors and liquid which are returned to tower 87 through line 92. Within the tower the vapors are separated from the liquid and a portion of them taken as product by way of line 93, while the remainder pass upwardly through the rectifying steps of the tower in vapor-liquid contact with the downflowing reflux liquid. The unvaporized material from line 92 commingles with the oxygen-rich liquid at the bottom of tower 87 and subsequently is recirculated through the adsorption circuit. When a liquefied oxygen-rich product is desired the bottom product of the rectification may be removed by way of line 94 instead of line 93 and the operating conditions of the air separation plant readjusted to supply the air to inlet line 83 at the proper temperature to maintain the described flow procedure.

The process arrangement diagrammatically shown by Figure 6 is essentially the same as that just described for Figure 5. It differs therefrom in that a portion of the partially liquefied feed air to rectifying tower 87 is totally liquefied in a bottom section of the tower by heat exchange relation with the liquid bottom product of rectification in reboiler 95. The liquid air thus obtained is thereafter taken through line 96 and combined with the liquid air passing through line 85 from reboiler 84. Optionally, the liquefied air in line 95 may be separately introduced into the top of tower 87 through a separate expansion valve. In this arrangement, part of the vapors from the oxygen-rich liquid at the base of the tower are produced by an inside reboiler 95 and the remainder in the outside reboiler 84 which functions in the manner as described for outside reboiler 31 of Figure 1.

The oxygen-rich product again may be withdrawn either in the liquid phase through line 94 or in the vapor phase through line 93, the conditions of operation being suitably adjusted for producing either type of product.

Having thus described my invention, what I claim and desire to secure by Letters Patent is:

1. In the fractionation of air, containing acetylene as an impurity, by liquefaction and rectification at relatively low temperatures, wherein oxygen-rich liquid is continuously added to a pool in the bottom of a rectification zone, and continuously reboiled from said pool, a method for preventing explosions which comprises: continually circulating a stream of liquid containing dissolved acetylene from said pool through a body of acetylene adsorbent material to remove dissolved acetylene, and back to said pool at a rate at least equivalent to the amount of liquid vaporized by the reboiling of said pool, and sufficient to maintain the acetylene in said pool at less than saturation, thereby preventing the existence of acetylene crystals in contact with said pool.

2. In the fractionation of air, containing acetylene as an impurity, by liquefaction and rectification in two stages at low temperatures, wherein said air is fractionated in a first stage under substantial pressure into a substantially pure nitrogen vapor fraction and a liquid fraction of increased oxygen and acetylene concentration, and wherein said liquid fraction is fractionated in a second stage under lower pressure into vapor fractions which are rectified in a rectification zone above a reboiling pool of liquid oxygen contain-

ing dissolved acetylene in still higher concentrations than in said first stage, the method of preventing explosions which comprises: continually circulating a stream of liquid oxygen, containing dissolved acetylene, from said reboiling pool through a body of acetylene adsorbent material and back to said pool at a rate of liquid flow not less than the rate of vaporization from said reboiling pool and sufficient to maintain the acetylene concentration within said reboiling pool below saturation, thereby preventing the existence of acetylene crystals in contact with said pool.

3. The method in accordance with claim 1 in which the acetylene adsorbent material comprises silica gel.

4. In the fractionation of air containing acetylene as an impurity, wherein compressed air is rectified in a first rectification stage into an oxygen-enriched liquid fraction and a substantially pure nitrogen fraction, wherein the fractions are again rectified together under lower pressure in a second rectification stage and a liquid predominantly oxygen rectification product containing dissolved acetylene is passed into a liquid body thereof in a lower part of the second rectification stage for reboiling by heat supplied by condensation of the substantially pure nitrogen fraction of the first rectification stage; the improvement which comprises continuously withdrawing portions of said liquid body, passing the withdrawn portions by gravity flow through silica gel to a second body of the liquid predominantly oxygen rectification product externally positioned with respect to said rectification stages thereby adsorbing dissolved acetylene from the withdrawn portions, reboiling and partially vaporizing said second liquid body by condensing at least part of the substantially pure nitrogen fraction to produce an outflowing overhead mixture of vapors and liquid from said second liquid body sufficient to establish and maintain the gravity flow of the withdrawn portions through the silica gel, and continuously returning unvaporized portions of the outflowing mixture from said reboiled second liquid body to the first mentioned liquid body of the liquid predominantly oxygen rectification product and thereby preventing precipitation of solid particles of acetylene from the liquid body of predominantly rectification product during the reboiling thereof.

5. In the fractionation of air, containing acetylene as an impurity, wherein compressed air is rectified to produce an oxygen-enriched air fraction and a substantially pure nitrogen fraction, wherein the fractions are again rectified together under lower pressure with the collection and reboiling of a liquid body of oxygen-rich liquid containing dissolved acetylene and the heat for reboiling is supplied by condensing vapors of the substantially pure nitrogen fraction; the improvement which comprises continuously passing a stream of oxygen-rich liquid from the liquid body through acetylene-adsorbent material at a rate not less than the rate of collection of oxygen-rich liquid in said body whereby the adsorbent removes dissolved acetylene from the stream at least at the same rate at which acetylene is entering the liquid body, then separately heating the purified oxygen-rich liquid of said stream by a separate heat exchange with a controlled amount of vapors of the substantially pure nitrogen fraction and vaporizing enough of the liquid of said stream to effect by thermal syphon

flow passage of the stream of oxygen-rich liquid through the adsorbent material at said rate not less than the rate of collection, and thereafter returning to said liquid body of oxygen-rich liquid being reboiled an unvaporized portion of the oxygen-rich liquid from said separate heat exchange in an amount and at an acetylene concentration sufficient to maintain the acetylene concentration in the liquid body below the acetylene saturation point thereby preventing precipitation of solid particles of acetylene from said liquid body.

6. In the fractionation of air, containing acetylene as an impurity, wherein compressed air is rectified to produce an oxygen-enriched air fraction and a substantially pure nitrogen fraction, wherein the fractions are again rectified together in a rectification zone under lower pressure with the collection of an oxygen-rich liquid containing dissolved acetylene; the improvement which comprises maintaining a body of the oxygen-rich liquid in said lower pressure rectification zone, continuously passing a stream of oxygen-rich liquid, containing dissolved acetylene, from the liquid body at a rate not less than the rate of collection thereof through acetylene-adsorbent material to adsorb dissolved acetylene, passing the purified stream of oxygen-rich liquid to a second liquid body, heating the second liquid body of oxygen-rich liquid by heat exchange with vapors of the substantially pure nitrogen fraction in a heat exchange zone externally positioned with respect to said lower pressure rectification zone, vaporizing at least enough of the liquid of the second liquid body to carry a mixture of vapors and liquid overhead therefrom sufficient to effect movement and passage by thermal syphon flow of said stream of oxygen-rich liquid through the adsorbent material at said rate not less than the rate of collection, thereafter separating from said mixture an unvaporized portion of oxygen-rich liquid and passing it to said first-mentioned liquid body of oxygen-rich liquid in an amount and at an acetylene concentration sufficient to maintain the acetylene concentration in the first-mentioned liquid body below the acetylene saturation point thereby preventing precipitation of solid particles of acetylene from said first-mentioned liquid body.

7. In the fractionation of air, containing acetylene as an impurity, wherein compressed air is rectified to produce an oxygen-enriched air fraction and a substantially pure nitrogen fraction, and wherein the fractions are again rectified together under lower pressure with the collection of a liquid body of oxygen-rich liquid containing dissolved acetylene which body is reboiled by heat supplied from condensing vapors of the substantially pure nitrogen fraction to produce a vaporous oxygen-rich rectification product and vapors for the last-mentioned rectification; the improvement which comprises continuously passing oxygen-rich liquid from said body through an acetylene-selective adsorbent material at a rate not less than the rate of said collection of oxygen-rich liquid from the second-mentioned rectification and sufficient to adsorb at least two parts of acetylene per million parts of oxygen-rich liquid passed, then separately heating the passed oxygen-rich liquid by a separate heat exchange with a controlled amount of vapors of the substantially pure nitrogen fraction and vaporizing enough of the last-mentioned reboiling

liquid to produce an outflowing mixture of vapors and liquid and effect by a thermal syphon flow the passage of oxygen-rich liquid from said body and through the adsorbent material at said rate, separating liquid portion of oxygen-rich liquid from the outflowing mixture, and introducing the liquid portion into said body in an amount and at an acetylene concentration sufficient to maintain the acetylene concentration in said body below about three parts of acetylene per million parts of oxygen-rich liquid thereby preventing precipitation of solid particles of acetylene from said liquid body during the reboiling thereof.

8. In the fractionation of air, containing acetylene as an impurity, wherein air is rectified into nitrogen-rich and oxygen-rich vaporous output products by reboiling vapors from a body of oxygen-rich liquid, in a lower portion of the rectification zone, the method of preventing the precipitation of acetylene crystals from said liquid body which comprises continuously removing a stream of oxygen-rich liquid containing dissolved acetylene from said body, continuously passing the removed stream through an acetylene-selective adsorbent material at a rate not less than the rate of vaporization from said oxygen-rich liquid body to continually adsorb dissolved acetylene from the stream, heating the thus purified oxygen-rich liquid of said stream by heat exchange with an inflowing stream of partially condensed air under higher pressure passing to said rectification zone in a heat exchange zone externally positioned with respect to said rectification zone, vaporizing enough of the purified liquid to produce an outflowing mixture of vapors and liquid sufficient to supply the vaporous oxygen-rich output product and vapors for said rectification and to effect by a thermal syphon flow the passage of the stream withdrawn from the liquid body through the adsorbent material at said rate, separating a liquid portion of oxygen-rich liquid from the outflowing mixture and introducing the liquid portion into said body in an amount and at an acetylene concentration sufficient to maintain the acetylene concentration in the liquid body below the acetylene saturation point therein.

9. In the fractionation of air, containing acetylene as an impurity, wherein partially condensed compressed air is rectified in a first rectification stage into a liquid oxygen-enriched fraction and a substantially pure nitrogen fraction, wherein the fractions are again rectified together under lower pressure in a second rectification stage with the collection and reboiling of an oxygen-rich liquid containing dissolved acetylene by heat supplied from condensing vapors of the substantially pure nitrogen fraction in the first rectification stage to produce a vaporous oxygen-rich rectification product and vapors for the second stage rectification; the improvement which comprises withdrawing from the liquid body collected under lower pressure a stream of oxygen-rich liquid containing dissolved acetylene, passing the withdrawn stream under thermal syphon flow conditions at a rate not less than the rate of vaporization from said liquid body through an acetylene-selective adsorbent material to adsorb dissolved acetylene from said stream, then passing the thus purified oxygen-rich liquid of said stream in heat exchange with a separate stream of partially condensed compressed air passing to the second rectification stage in a heat exchange zone externally positioned with respect to said

second rectification stage, thereafter combining the separate stream of partially condensed compressed air with a stream of the liquid oxygen-enriched fraction of the first rectification stage and expanding the combined streams into said second rectification stage, vaporizing enough of the purified oxygen-rich liquid in the heat exchange zone to produce an outflowing mixture of vapors and liquid to establish and maintain the thermal syphon flow of the withdrawn stream at said rate, separating liquid portion of oxygen-rich liquid from the outflowing mixture and introducing the liquid portion into the liquid body of oxygen-rich liquid being reboiled in the second rectification stage in an amount and at an acetylene concentration sufficient to maintain the acetylene concentration in the liquid body below the acetylene saturation point therein and thereby preventing precipitation of solid particles of acetylene from said liquid body during the reboiling thereof.

10. In the fractionation of air, containing acetylene as an impurity, wherein partially condensed compressed air is rectified in a first rectification stage into a liquid oxygen-enriched fraction and a substantially pure nitrogen fraction, wherein the fractions are again rectified together under lower pressure in a second rectification stage with the collection of a body of oxygen-rich liquid, containing dissolved acetylene in the second stage rectification; the improvement which comprises withdrawing from the liquid body in the second rectification stage a stream of the oxygen-rich liquid containing dissolved acetylene, passing the withdrawn stream through an acetylene-selective adsorbent material at a rate not less than the rate of said collection of oxygen-rich liquid in the liquid body to adsorb acetylene from the stream at least at the same rate at which acetylene is entering the liquid body, removing the purified oxygen-rich liquid stream from contact with the adsorbent material, separating from the purified stream a liquid oxygen-rich output product of the air fractionation, passing the remainder of the purified stream in heat exchange relation with vapors of the substantially pure nitrogen fraction of the first rectification stage to produce at least sufficient vapors for the second stage rectification, separating an unvaporized portion of the purified oxygen-rich liquid after the last-mentioned heat exchange and introducing said unvaporized portion into the body of oxygen-rich liquid in an amount and at an acetylene concentration sufficient to maintain the acetylene concentration in the liquid body below the acetylene saturation point therein and thereby preventing precipitation of solid particles of acetylene from said liquid body.

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