March 21, 1961 E. KARWAT 2,975,606

PROCEDURE FOR THE VAPORIZATION OF LIQUID OXYGEN WHICH CONTAINS HYDROCARBONS

Filed March 14, 1958 4 Sheets-Sheet 1

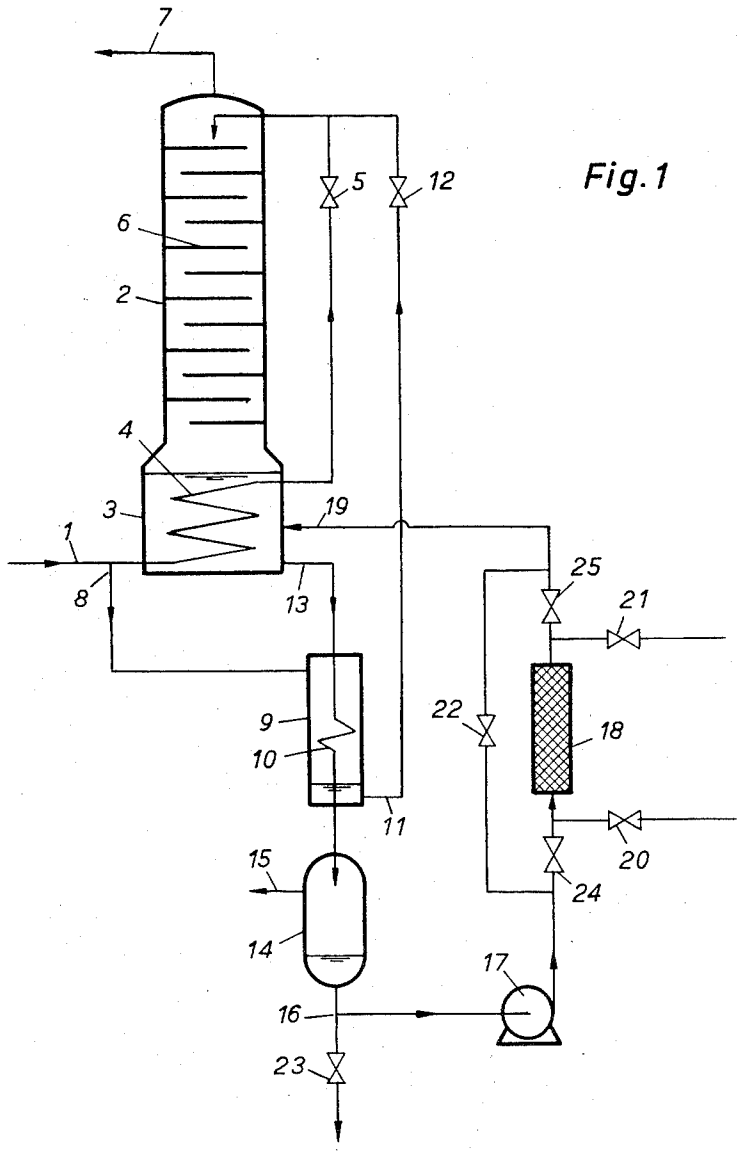


Fig. 1

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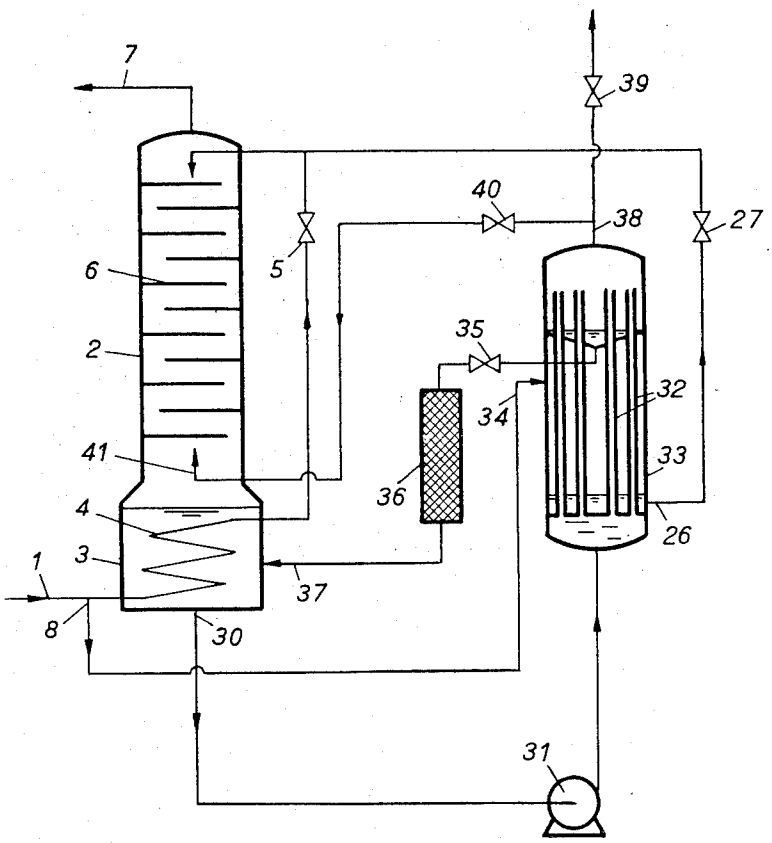


Fig. 2

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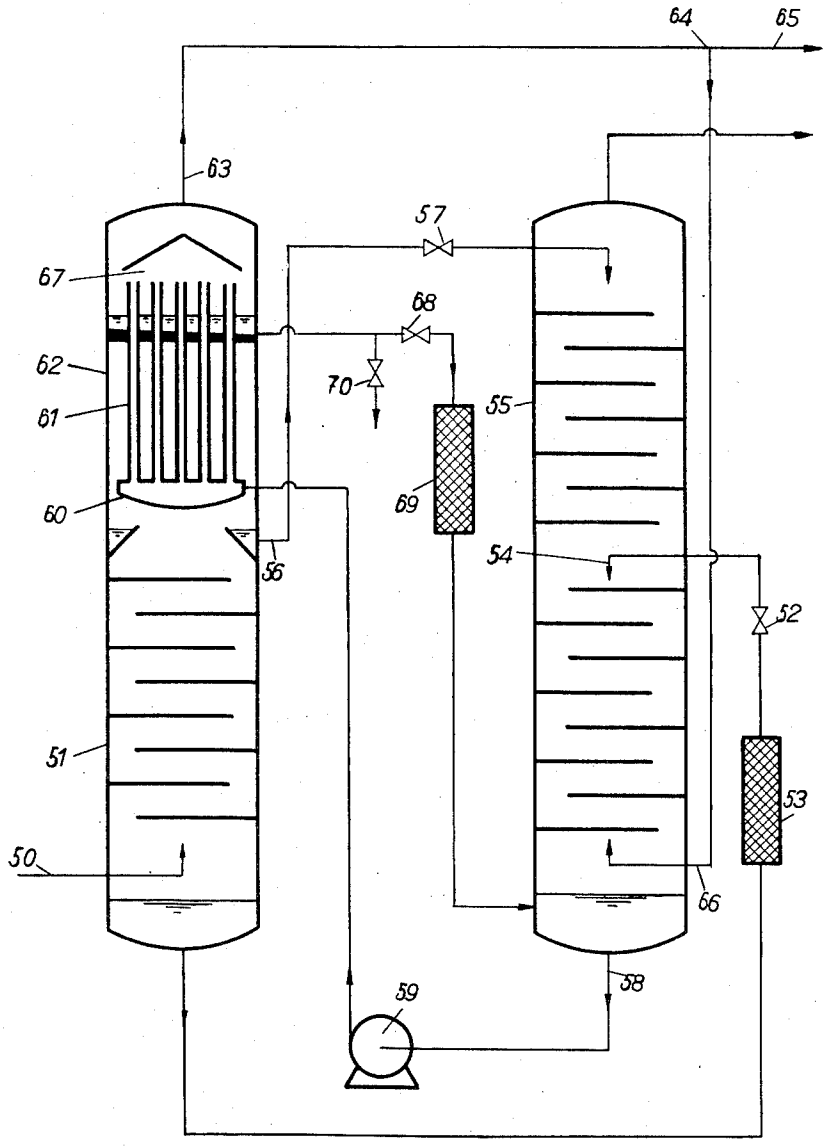


Fig. 3

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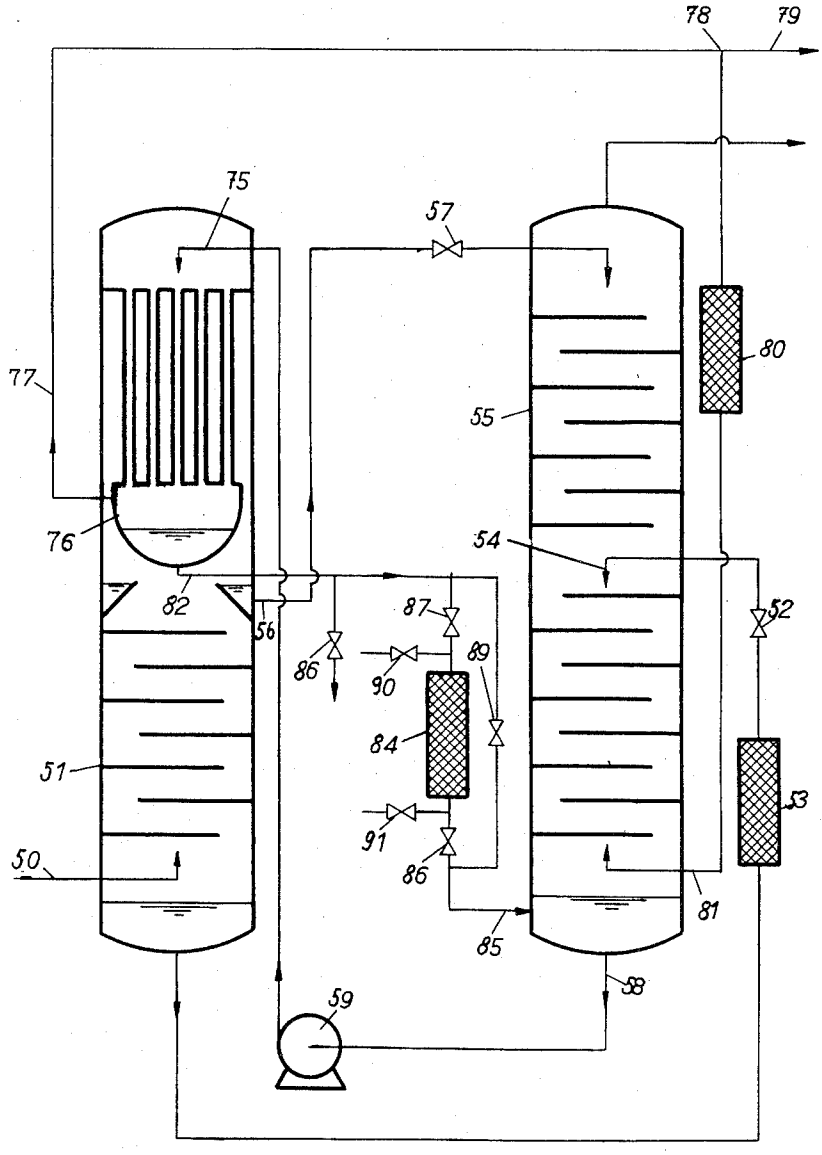


Fig. 4

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PROCEDURE FOR THE VAPORIZATION OF LIQUID OXYGEN WHICH CONTAINS HYDROCARBONS

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4 Claims. (Cl. 62—18)

Air separating apparatus, in which air is separated by liquefaction and rectification into nitrogen and oxygen, are known to be endangered through the unavoidable presence of hydrocarbons, such as acetylene or propylene, in the air. Despite the employment of the customary purification expedients, such as regenerators or acetylene adsorbers, hydrocarbons such as ethylene, ethane, propylene, propane, butylene and butane, as well as traces of acetylene, still enter the bath of the liquid oxygen of the main rectification column. A known measure for preventing greater accumulations of such hydrocarbons in the bath of liquid oxygen flowing around the main condenser at the foot of the rectifying column consists in withdrawing the quantity of oxygen to be produced from the bath in liquid form and vaporizing it into gaseous form, outside the bath, in an auxiliary vaporizer in an equal stream with the vapors formed. The gaseous oxygen is led to the heat exchanger. The auxiliary vaporizer consists of a series of pipes connected in parallel, which are surrounded on the outside by a gas, such as air or nitrogen, under pressure. This gas condenses and thereby gives off the heat needed for the vaporization of the liquid oxygen inside the pipes. The hydrocarbons dissolved in the oxygen become enriched in the liquid phase during the vaporizing process. At such enrichment, the solubility limit of the hydrocarbons in the liquid must not be exceeded, for otherwise, explosion hazardous solid deposits would form in the auxiliary condenser. A further disadvantage is that one or the other of the pipes connected in parallel will occasionally become clogged with water ice or carbon dioxide ice. Liquid oxygen subsequently entering such a pipe is totally vaporized in it and hydrocarbons accumulate in this pipe in solid form. The result may be that it is destroyed by a hydrocarbon explosion and nitrogen then penetrates continuously into the oxygen. It is the custom to prescribe for the operation of the auxiliary vaporizer that a small fraction of the liquid to be vaporized is withdrawn at the lower end of the auxiliary vaporizer as a liquid in the form of an unsaturated solution. It is collected in a separator arranged behind the vaporizer, where it separates from the gas. It is brought to the outside. However, very narrow limits (0.1–1% of the oxygen production) are set for the withdrawal of liquid. A loss of 2% of liquid oxygen is already intolerable because it entails a loss of 10% of the total cold production.

When processing air which, apart from acetylene, has a high content of hydrocarbons such as propane and butane, it often happens that the customary acetylene adsorbers cannot prevent that the liquid oxygen at the bottom of the rectification column still contains appreciable quantities of such hydrocarbons. Then there exists the danger that, when vaporizing the liquid oxygen in the auxiliary vaporizer to a remainder of 0.5–1%, saturated solutions or solid deposits will occur. A far bigger remainder, e.g. 5%, should be left unvaporized. In such case, the loss in production and refrigeration will, however, exceed the tolerable degree. The object of the present invention is the provision of means for increasing the safety of handling of the auxiliary vaporizer and reducing the loss of oxygen and cold production. The procedure of the invention for the vaporization of hydrocarbon-containing liquid oxygen obtained by rectification of hydrocarbon-contaminated air in a rectifying column, in an auxiliary vaporizer consisting of a bundle of pipes connected in parallel, through heat exchange with a gas condensing outside on the bundle of pipes, with more liquid oxygen being led to the vaporizer than will be vaporized and the forming gaseous oxygen streaming in an equal stream with the vaporizing liquid, consists in that the unvaporized portion will be led back into the bath of liquid oxygen at the foot of the rectifying column.

In the auxiliary vaporizer the liquid and the gaseous oxygen are led in unidirectional flow preferably from top to bottom. The procedure of the invention, i.e. the refeeding of the unvaporized remainder of liquid into the bath of the main condenser, can also be carried through by passing liquid oxygen and gaseous oxygen together in the auxiliary vaporizer from bottom to top and by separating the excess liquid from the formed gas at the upper end of the auxiliary vaporizer and by passing the gaseous oxygen to the heat exchanger and the liquid back to the bath of the liquid oxygen at the foot of the rectifying column.

The unvaporized remainder of the liquid oxygen is highly enriched with less volatile hydrocarbons such as propane, butane. In order to remove them from the rectification system, the excess of liquid withdrawn from the auxiliary vaporizer will, according to a further step of the invention, be freed from hydrocarbons by means of an absorption agent prior to being led back to bath of the liquid oxygen at the foot of the rectifying column. Silica gel constitutes, for instance, a suitable adsorption agent.

A further step of the invention consists in that so much liquid oxygen will be vaporized in an unidirectional flow vaporizer operated as described, that together with the produced quantity of gaseous oxygen which will be passed to the heat exchanger, there will likewise be produced that quanity of gaseous oxygen which will be necsary for the rectification in the low-pressure column and which will therefore be led back to the rectification column whilst, if necessary, being freed from hydrocarbons by means of an adsorption agent such as silica gel.

This working method is chiefly used with the known system of air separators the pressure column and the low-pressure column of which are not arranged one on top of the other but side by side, with an exchanger-vaporizer being arranged at the top of the pressure column and a pump pumping liquid oxygen from the bottom of the low-pressure column to the vaporizer at the top of the pressure column.

The invention will be more readily understood from a study of the following specification when considered in conjunction with the accompanying drawings in which:

Fig. 1 is a diagrammatic illustration of a vaporizing apparatus and method according to the present invention;

Fig. 2 diagrammatically illustrates a unidirectional flow vaporizer embodiment;

Fig. 3 diagrammatically illustrates a unidirectional flow vaporizer in which the liquid and vapors rise together from bottom to top; and

Fig. 4 diagrammatically illustrates a top-to-bottom type of unidirectional flow vaporizer.

The air containing hydrocarbons, cooled down in heat exchange with its separation products oxygen and nitrogen, not shown, passes at 1 before the separation apparatus (Fig. 1) and there divides into two streams one of which condenses in the coil of pipe 4 of the vaporizer-condenser 3, located at the foot of the rectifying column 2, is expanded through the valve 5 to the head of the col-

umn 2 and is separated on the trays 6 of the rectifying column into liquid oxygen in the bath 3 and nitrogen which leaves in gaseous form at the head of the column at 7. About one-fifth of the hydrocarbon-containing air is branched off at 8 and led to the auxiliary vaporizer 9 where it liquefies on the outside of the bundle of pipes 10 through which liquid oxygen flows, is taken out at 11 and expanded through the valve 12 to the head of the column 2. From the bath of liquid oxygen in the main condenser 3, there is taken at 13 a weight of liquid oxygen greater by 10 to 50% or more than that of the gaseous oxygen to be produced. The liquid flows through the bundle of pipes 10 consisting of a large number of pipes connected in parallel, and is vaporized in the downward stream by the air condensed externally on the bundle of pipes, whereby the vapors are in unidirectional flow with the liquid. An unvaporized excess of 10 to 30% of the liquid separates in the separator 14 from the gaseous oxygen leaving at 15, and leaves the separator 14 at 16 and is led by the pump 17 over the adsorber 18, filled with silica gel, and by way of conduit 19 back to the main portion of the liquid oxygen in the bath 3. During the vaporization in the bundle of pipes 10 only a part of the hydrocarbons contained in the liquid goes into the gaseous phase, whereas the content of hydrocarbons in the liquid rises during the vaporization. In the adsorber 18, the hydrocarbons enriched in the liquid are bound to the silica gel by adsorption. After leaving the adsorbent, the returning liquid contains only traces of hydrocarbons. The adsorber 18, when charged with hydrocarbons, is expediently freed of the hydrocarbons which it has taken up, by heating and simultaneous rinsing with a dry gas, for example nitrogen, introduced at 20 and led off at 21. During this time, the liquid goes from the pump 17 through the bypass 22 and at 19 into the bath 3. From the separator 14, at 16, a small amount of hydrocarbon-rich liquid can be let into the outside through the valve 23 in order to support the purification of the cycle.

In Figure 2 is shown a unidirectional flow vaporizer through which the oxygen to be vaporized streams from bottom to top. In the figure the same numbers designate the same parts and same functions of the apparatus as in Figure 1, and hence need not be re-described.

In contrast to the procedure described with reference to Figure 1, liquid oxygen is here withdrawn at 30 from the bath of the main condenser by the pump 31 in an amount exceeding the oxygen to be vaporized, is led to the vertical bundle of pipes 32 of the auxiliary vaporizer 33 from below and there a part equal to the quantity of oxygen produced is vaporized through the condensation of air which enters the auxiliary vaporizer at 34 in gaseous form, leaves the auxiliary vaporizer at 26 totally liquefied and is expanded with the valve 27 into the upper column 2.

The quantity of gaseous oxygen produced leaves the auxiliary vaporizer 33 at 38 through the valve 39. The unvaporized excess of liquid oxygen leaves the auxiliary vaporizer 33 and goes through the valve 35 through the adsorber 36, then to return, purified, at 37 into the bath of liquid oxygen in the main condenser 3. As regards the purification which is effected in the adsorber 36, there applies the same thing as was said about the adsorber with reference to Figure 1, and likewise regarding the measures for the desorption of the adsorbent in the adsorber 36, which are not represented in Figure 2.

The auxiliary vaporizers according to the figures can also be so operated that more than the quantity of oxygen produced is gasified in them, in the limiting case such that the quantity of oxygen required for the rectification is also formed together with that to be produced. The excess of gasified over product oxygen is then introduced into the rectifying column 2 through the valve 40 at 41 in the case of Figure 2. Under such conditions the quantity of liquid oxygen withdrawn at 30 must not only be greater than the quantity of oxygen produced by that part of the liquid which remains unvaporized but also by the amount of gaseous oxygen which is led back into the rectifying column at 41.

No limitation of the liquid excess is to be implied in the figures mentioned in the examples. It is open to anyone, within the frame of the inventive idea, to allow smaller or greater excesses of liquid to circulate, for example, three times the oxygen production.

Usually, air is preseparated in a pressure column and rectified to completion in a low-pressure column heated with pressure column nitrogen. If the inventive idea is applied in such a system, then the auxiliary vaporizers 9 or 33 as well as the bath of liquid oxygen in 3 are heated not with air but with condensing pressure column nitrogen.

The example according to Figure 3 refers to a unidirectional flow vaporizer in which liquid and vapors rise together from bottom to top, while the example according to Figure 4 refers to a unidirectional flow vaporizer of the top-bottom type. Both examples, 3 and 4, refer to air separation plants the pressure column and the low-pressure column of which are arranged side by side.

In Figure 3, compressed air pre-cooled in the heat exchanger (not shown) enters into the pressure rectifying column 51 at 50; the oxygen-rich liquid produced here passes through the valve 52 and silica gel adsorber 53 into the low-pressure column 55 at 54. Liquid nitrogen withdrawn from the pressure column at 56 is admitted behind the valve 57 to the head of the low-pressure rectifying column 55. The liquid, hydrocarbon-containing oxygen formed by rectification in the low-pressure column is withdrawn at 58 at the foot of the low-pressure column and led by the pump 59 to the bottom of the vaporizer 60 placed on the head of the pressure column 51, flows upward in the bundle of pipes 61 and is partly vaporized during this time by condensation of nitrogen flowing in the upper part 62 of the pressure column 51. The vaporized oxygen leaves the separating chamber 67 arranged above the unidirectional flow vaporizer 61 at 63 and divides into two streams at 64. The quantity of oxygen equal to the product goes in the direction 65 to the heat exchanger (not shown). The quantity of oxygen needed to charge the low-pressure column—about four times the production quantity—goes at 66 above the bath of liquid oxygen into the low-pressure column 55. It can be cleansed of hydrocarbons in an adsorber (not shown) between 64 and 66.

More liquid oxygen is introduced at the bottom of the vaporizer 60, by pump 59, than is vaporized. The excess of liquid oxygen, enriched with hydrocarbons, separates from gaseous oxygen in the separating chamber 67, flows through the valve 68 and, after purification in the silica gel adsorber 69, back into the suction line of the pump 59 or, as shown, into the bath of liquid oxygen at the foot of column 55. At the valve 70 there is provided an outlet into the open air, through which a small amount of contaminated liquid can be drained if necessary.

In Figure 4 is shown a unidirectional flow vaporizer through which flows the oxygen to be vaporized, together with the vapors formed, from top to bottom. In the figure the same numbers designate the same parts and functions of the apparatus as in Figure 1, and hence need not be re-described.

In contrast with the procedure described in reference to Figure 3, the liquid oxygen withdrawn at 58 from the low-pressure column is led by the pump 59 to the upper end of the unidirectional flow vaporizer at 75, in which vaporized liquid oxygen and the vapor formed go downward to the separator 76, from where the vapors formed go into the line 77 and to the point of distribution 78.

The quantity of oxygen corresponding to the production goes to the heat exchanger in the direction 79, while the quantity of oxygen required for charging the rectifying column—if necessary purified in the adsorber 80—

enters at 81 below the trays of the low-pressure column.

The liquid collected in the separator 76 is withdrawn at 82, led back through the valve 87 and through the adsorber 84 into the bath of liquid oxygen at the foot of the low-pressure column at 85. Outlet valve 86 functions for the removal of small quantities of liquid for the purpose of diminishing the quantities of hydrocarbons present in the system. Valves 87—91 are provided in a manner known per se for the desorption of the adsorber 84.

It is in the frame of the invention to make use of all known measures to reduce the hydrocarbon danger, e.g. to provide self-cleaning regenerators as heat exchangers for the cooling of the air and/or silica gel adsorbers for the purification of the oxygen-rich liquid between the pressure column and the upper column.

The working method according to the invention thus offers a much higher degree of safety against explosions of hydrocarbons in liquid oxygen, and is capable of processing considerably larger quantities of hydrocarbons in the processed air, without danger.

With reference to the procedure according to the invention and to the described examples it is characteristic that unidirectional flow vaporization in the auxiliary vaporizer and re-feeding of an excess of liquid oxygen from the auxiliary condenser to the bath of the liquid oxygen at the foot of the rectifying column are combined. This combination is novel. Contrary to the hitherto known working methods, only this combination secures, without danger, the positive removal of large quantities of hydrocarbons in liquid oxygen from the air separation system. The unidirectional flow of vaporizing liquid and the forming of vapor in auxiliary vaporizers is known and customary in technology; the practice of feeding somewhat more liquid to the auxiliary vaporizer than is vaporized is known, moreover, with the limitation that, for reasons of rentability and productive capacity, this rest of liquid must not exceed 0.1–1% of the production which is insufficient for the handling of larger quantities of hydrocarbons. The novelty of the present invention lies in pumping this remainder of liquid in by far greater quantities back to the rectification column.

It is also known, in the case of air separation plants where pressure column and low-pressure column are arranged side by side, to feed oxygen by means of a pump from the foot of the low-pressure column to the vaporizer-condenser located at the head of the pressure column; however, in this known vaporizer, the liquid to be vaporized and the forming vapor travel in countercurrent, this however results in that both the liquid and the gaseous oxygen which is led back from the vaporizer to the low-pressure column, become continually enriched in hydrocarbons. Thus, the low-pressure column is charged with extremely high acetylene- and hydrocarbon concentrations both at the foot and on the rectification trays arranged above. These drawbacks are eliminated if the inventive idea i.e. the method of unidirectional vaporization is employed. The procedure according to the invention offers a much higher degree of safety.

I claim:

1. In the fractionation of air containing hydrocarbons as impurities by liquefaction and rectification under relatively low temperatures, wherein compressed air is rectified in a first rectification stage into an oxygen-enriched liquid fraction and a substantially pure nitrogen fraction and wherein the said oxygen-enriched liquid fraction is partially purified from hydrocarbons by passing through an adsorber and wherein the fractions are again rectified together under low pressure in a second rectification stage and wherein a liquid oxygen product containing dissolved hydrocarbons is passed into a liquid body thereof in a lower part of the second rectification stage; the improvement which comprises continuously withdrawing a portion of said liquid body, passing the withdrawn portion into a vaporizer in the top of said first rectification stage, partially vaporizing said liquid by heat supplied by condensation of the substantially pure nitrogen fraction of the first rectification stage, separating the unvaporized portion of said liquid from said vapors, withdrawing said gaseous portion and passing part of it into the lower section of the low pressure column and withdrawing the other part as a product, recirculating said unvaporized liquid portion at a rate of less than 30% of the amount of liquid vaporized and withdrawn as a product through a body of adsorbent material thereby adsorbing dissolved hydrocarbons, and back to said liquid body.

2. In a process according to claim 1 in which said part of said gaseous portion withdrawn from the vaporizer and led to a lower section of the low pressure column is passed through a body of adsorbent material.

3. Apparatus for producing gaseous oxygen from hydrocarbon-contaminated air which comprises a high pressure rectification column, a vaporizer situated in the head of said column, a low pressure rectification column, conduit means from the bottom of said high pressure column to an adsorber, valve fitted conduit means from said adsorber to a medium section of said low pressure column, means including a pump connecting the bottom of the low pressure column with the lower end of said vaporizer, means connecting the pool of the hydrocarbons-containing liquid oxygen in said vaporizer with a second adsorber and means connecting said second adsorber with the lower section of the low pressure column, means for withdrawing the gaseous oxygen from said vaporizer as a product and means for passing gaseous oxygen from said vaporizer to a lower section of the low pressure column, means for collecting liquid nitrogen in the head of the high pressure column and means for conducting said liquid nitrogen to the head of the low pressure column, and means for withdrawing gaseous nitrogen from the head of low pressure column.

4. Apparatus as claimed in claim 3 in which an adsorber is connected in the means for passing gaseous oxygen from the vaporizer to the lower section of the low pressure column.

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