July 24, 1934. L. J. BOWDITCH 1,967,736

PROCESS OF PURIFYING GAS MATERIAL

Filed April 23, 1932 2 Sheets-Sheet 1

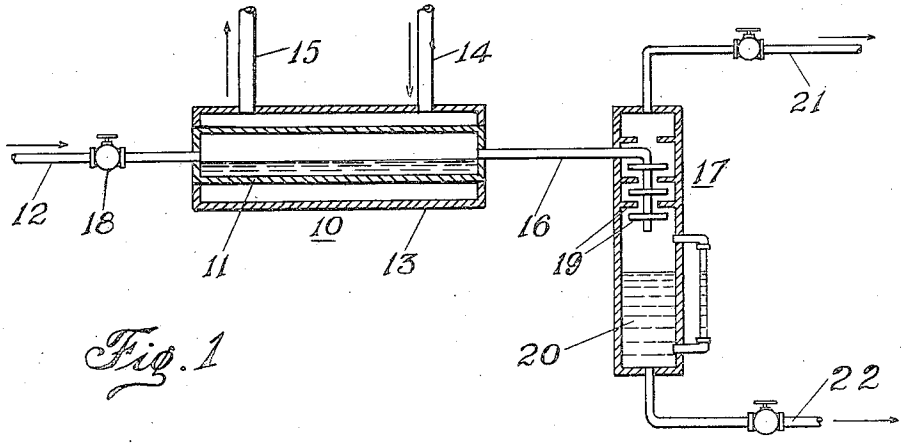

Fig. 1

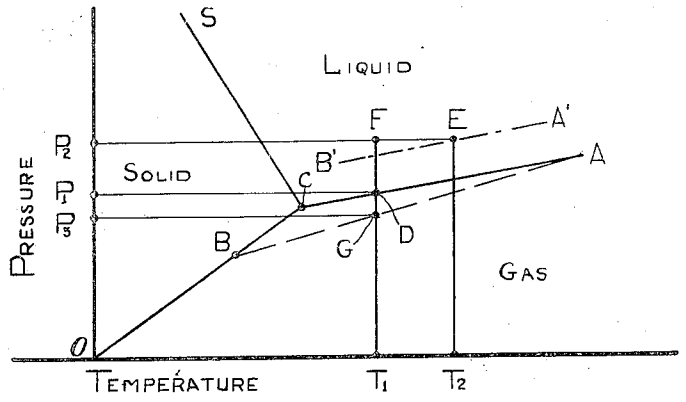

Fig. 2

INVENTOR
Lawrence J. Bowditch
BY
Watson, Bristol, Johnson & Leavenworth
ATTORNEYS

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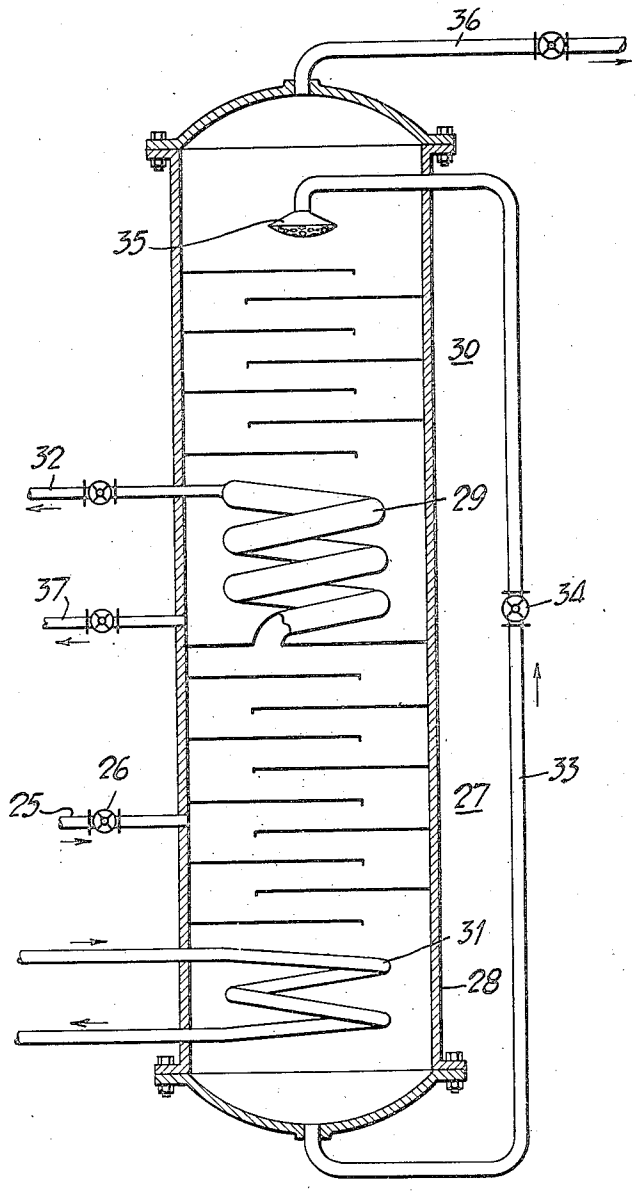
Fig 3.



INVENTOR
Lawrence J. Bowditch
BY
Watson, Bristol, Johnson & Leavenworth
ATTORNEYS

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PROCESS OF PURIFYING GAS MATERIAL

Lawrence J. Bowditch, Flushing, N. Y., assignor, by mesne assignments, to The Linde Air Products Company, New York, N. Y., a corporation of Ohio

Application April 23, 1932, Serial No. 607,074

3 Claims. (Cl. 183—115)

This invention relates to a process of purifying gas material and particularly gas material which has been collected as a by-product and contains one or more undesired impurities, and has for its object generally an improved procedure whereby such impurities are readily and expeditiously removed.

More specifically, the invention relates to the removal of impurities which occur in relatively small amounts in liquefied gases, such as liquefied air, oxygen, carbon dioxide, and the like, their concentrations being such as a rule that they do not materially change the boiling point of the liquefied gas, but are otherwise objectionable and impair the commercial qualities of the gas product.

A specific object is to accomplish the substantially complete removal of these impurities with a relatively small expenditure of energy and at relatively little cost.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others thereof, which will be exemplified in the process hereinafter disclosed, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention reference should be had to the following detailed description taken in connection with the accompanying drawings, in which:

Fig. 1 is a view mainly in vertical section showing a simple form of apparatus adapted for carrying out the process of the present invention;

Fig. 2 is an explanatory diagram; and

Fig. 3 is a view mainly in vertical section showing apparatus for removing more than one variety of impurity, in accordance with the present invention.

In the commercial production of liquefied gases, undesirable impurities are generally present, both by reason of the sources from which the gas is obtained and on account of the manufacturing steps commonly employed to produce initially the liquid state or phase. Such impurities, though present even in so small an amount as not to change appreciably the boiling point of the liquefied gas, are detectable in the final product, and are commercially objectionable. This is particularly true in the production of liquefied gases, such as liquid air, liquid oxygen and liquid carbon dioxide.

These impurities have heretofore been removed to a certain extent by passing the gas material over activated carbon, silica gel or activated alumina. The use of such agents, however, has proved to offer considerable difficulty as a commercial method for continuously removing all such impurities. The renewal of these agents also involves a considerable item of expense.

Certain types of undesired impurities so incorporated with the gas material in commercial practice are less volatile than the gas material, that is, having melting points materially above the boiling point of the gas material. To accomplish the removal of these less volatile impurities, in accordance with the present invention, gas material which contains the undesired impurities is brought to a condition by the step of fractional evaporation, under conditions of temperature and pressure where the vapor pressure of the impurity is of negligible value (i. e., a value, which when expressed in customary units is of an order practically incapable of measurement in commercial practice), such that separation may be produced physically, the impurities remaining in the liquid or solid phase. The purified gas fraction is then separated therefrom in any convenient state, for example in the gas phase.

Where the gas material initially contains various impurities, some of which are more volatile and others less volatile than the gas material, the purifying process of the present invention may be practiced in two stages, in the first of which the more volatile impurities are drawn off in the gas phase, so that the liquid fraction remaining comprises not only the desired gas material, but also the less volatile impurities. In the second stage, fractionation is practiced as before, whereby the purified gas material may be withdrawn in the gas phase.

In order that this purifying process may be practiced with the expenditure of relatively little energy, the gas material which contains the undesired impurities is passed into a heat exchanger and brought substantially to a condition where the less volatile impurities tend to separate out in their liquid or solid phases. Hence, the fractionation desired may be obtained merely by the exchange of a certain amount of latent heat to produce the phase change involved.

Referring now to the drawings and particularly to Fig. 1, 10 denotes generally a heat exchanger having a chamber 11 supplied with the gas material through the conduit 12. A heat exchanging jacket about the chamber 11 is shown at 13, provided with inlet and outlet connections 14 and 15, respectively. The chamber 11 has an outlet con-

duit 16 leading to the phase separator shown generally at 17.

The flow of gas material, containing impurities which are less volatile than the pure gas material, through conduit 12 into the chamber 11 is controlled by valve 18. In chamber 11 it is subjected to such temperature and pressure conditions by means of heat exchange, expansion, and the like, that a resulting mixture of two or more phases is obtained; such treatment being effected by an agent, such as heat bearing compressed gas taken from another portion of the manufacturing cycle that is circulated in the jacket 13 to supply heat. When the gas material in chamber 11 obtains sufficiently in the gas phase, it passes over together with the less volatile impurities into the separator 17; the impurities tending to concentrate in the liquid and solid phases. Here the liquid phase falls by gravity to the bottom of the separator, as shown at 20, while the gas phase passing up through the baffles 19 finds exit through the conduit 21. The liquid and solid phase at 20 accumulates the impurities which are less volatile than the liquid phase of the gas material, so that a withdrawal conduit 22 is provided for the separator at its lower end whereby this liquid may be withdrawn when desired.

For the purposes of the invention it would be equally practical to supply refrigeration in chamber 11 by a direct admission of the cooling medium through line 14 into chamber 11. Thus a certain portion of the gas material in liquid form might be expanded directly into chamber 11, thus providing the necessary cooling effect for partial condensation, without the use of indirect heat exchange equipment.

The practice of the process of the present invention by means of the apparatus illustrated in Fig. 1 will be more readily understood by reference to the phase diagram in Fig. 2, which is drawn with temperatures as abscissae and pressures as ordinates. Here, the line OC denotes the solid-gas equilibrium curve for the gas material to which the process is applied, C denoting the triple point. CA, likewise, denotes the liquid-gas equilibrium curve, while CS denotes the liquid-solid equilibrium curve. Where the gas material contains a less volatile impurity, for example, an odorous impurity, its liquid-gas equilibrium curve would, in general, fall below the liquid-gas curve for the gas material itself when drawn on the same chart. The broken line BA is drawn to represent such a curve for the impurity.

If, therefore, gas material containing a small but nevertheless objectionable quantity of less volatile impurities is admitted to chamber 11 at a pressure P_1, such material would be in the gas phase if above the temperature T_1, and would be in the liquid phase if at a temperature lower than T_1. Whatever the initial condition of the gas material entering chamber 11, however, a transfer of heat may be effected such that a portion of the gas material may be vaporized, whereby the resulting mixture may contain both liquid and gaseous phases. Whereas, this gas material may contain certain less volatile impurities which have a liquid gas equilibrium curve such as BA considerably below the gas material itself, it is obvious that such impurities may separate out into either the liquid or solid phase at a temperature considerably higher than the temperature T_1 at which the gas material itself may condense at a given pressure P_1. Due to the difference in liquid-gas equilibrium curves between the gas material and its less volatile impurities, therefore, heat transfer may be effected in chamber 11 such that a mixture of two or more phases may be obtained in substantial equilibrium, such that the less volatile impurities tend to separate out almost entirely in the liquid or solid phase, leaving the gaseous phase in a state of almost complete freedom from these impurities. Such a separation might even be accomplished at a temperature considerably above the condensation temperature T_1 of the gas material, or might be accomplished at the temperature T_1 in which case a portion of the gas material itself might be actually condensed into the liquid phase. The optimum operating conditions must depend upon the nature of the gas material and the impurities, and the relative ease with which the impurities may be separated into the liquid or solid phases.

The gas and liquid or solid phases are therefore readily separated in separator 17, and hence any material withdrawn through the conduit 21 is the gas material in a gas phase in the purified condition desired. The material withdrawn through the conduit 22, therefore, contains substantially all the undesired impurities, this material being withdrawn at will from the separator. Since it may be desired to avoid undue accumulation of material in the separator, the latter is preferably provided with visual means such as a gauge glass whereby the total liquid content of the separator may be ascertained whenever desired.

Where the undesired impurities represent an aggregate of those both more and less volatile than the gas material itself, an arrangement of apparatus for practicing the purification steps of the present invention in two stages is shown in Fig. 3. Here, the gas material containing the undesired impurities is supplied through a conduit 25 having a controlling valve 26, for example, an expansion valve, and passed into a rectifying column shown generally at 27. This column has a vaporizer or kettle 28 at its lower end, and is supplied with a condenser 29 at its upper end. This column is arranged to rectify the liquid whereby the gas fraction constituting the undesired more volatile impurities is first withdrawn. Surrounding the condenser and preferably superposed above the column 27 is a second rectifying column 30 for effecting the second stage of purification. These two rectifying columns may have any suitable construction and are provided with counter-current surface contact means of any suitable variety, that are here illustrated comprising perforated trays. The rectification accomplished by the column 30 is seen also to set free a gas fraction, which, as in the form shown in Fig. 1, is the purified gas fraction desired.

In the arrangement last shown, it is seen that, when the gas material supplied through the conduit 25 enters the column 27 in the liquid phase, it will collect in the vaporizer at 28, which is preferably provided with a heating coil 31 in order that there may be supplied slowly a relatively small amount of heat to the liquid therein from which distills off a gas fraction including the more volatile impurities that rise through the column into the condenser 29. Here, the desired gas material is recondensed and caused to flow back to the vaporizer 28, while the more volatile impurities are withdrawn in the gas phase through the conduit 32 from the top of the condenser.

The second stage of purification accomplishes

the removal of the less volatile impurities by inducing rectification and separation in column 30. This column is supplied with liquid from the vaporizer 28, which contains the less volatile impurities that are withdrawn through the conduit 33 and enters the rectifying column 30 at the top and is provided with an expansion valve 34 and a distributor 35. The rectification accomplished in the column 30 is so arranged with respect to that taking place in the column 27 that the liquid phase descending in column 30 is brought into thermal contact with the ascending vapors in the column 27, whereby a heat transfer takes place between the ascending vapors in column 27 and the gas material in column 30. This heat transfer may be effected by maintaining the pressures and temperatures in column 30 lower than those in column 27. Hence, the prevailing temperature in the bottom of the column 30 is colder than the existing temperature of the ascending vapors in the top of the column 27, with which the liquid is brought into thermal contact. The heat transfer, which in consequence takes place, results in vaporizing the liquid in the bottom of the column 30 about the condenser. Rectification then follows and a concentration of liquid containing the undesired less volatile impurities gathers in the column 30 about the condenser 29, while a gas fraction uncontaminated by a less volatile impurity is withdrawn through a conduit 36 leading from the top of the column 30. The liquid phase in the bottom of the column 30 is withdrawn at will through a conduit 37.

The manner in which this two stage practice of the present invention operates will also be readily understood by reference to the phase diagram in Fig. 2. Here, the point E on the liquid-gas equilibrium curve A'B' represents a certain condition of the more volatile undesired impurities in the gas material, which enter the column 27. This point E, corresponding to a pressure P_2 and a temperature T_2 may obtain in the column 27 when this material is introduced and collected in the evaporator 28, and is here taken as exemplary. By supplying heat to the liquid through the instrumentality of the coil 31, the volatile constituent is vaporized, together with a small portion of the gas material which passes upwardly in the rectification column, the latter being readily condensed in the condenser 29, so as to return to the vaporizer 28. The uncondensed volatile fraction produced being withdrawn through the conduit 32.

The pressure P_1 on the diagram may be taken as indicating the pressure in the column 30, so that there is a pressure differential corresponding to $P_2—P_1$ causing a flow of the liquid from the evaporator 28 into the top of the column 30. This liquid passing through the expansion valve 34 also undergoes a temperature drop so that the gas material when it reaches the bottom of the column 30 is in the condition indicated by point D on the diagram. Here, it is seen that the heat supplied by the condenser 29 in refrigerating the material in column 27 produces gas material in two phases in the column 30 without vaporizing the less volatile constituent comprising the undesired impurity. A pure gas fraction, in consequence, is withdrawn through the conduit 36, whereas liquid with an accumulated amount of the impurity is withdrawn through the conduit 37.

The present invention is particularly advantageous in connection with the commercial production of the so-called "permanent" gases, such as oxygen and nitrogen, in substantially pure condition, and is also advantageous in connection with the commercial production of carbon dioxide, from which odorous impurities have heretofore been removed only with difficulty and comparatively great expense. The odorous impurities which are particularly objectionable from a commercial standpoint have been ascertained to belong substantially to the class of the less volatile impurities indicated above, and are hence readily removed by the process of the present invention.

The phrase "gas material" is used herein to denote generically a substance that under standard conditions (i. e., under a pressure of one atmosphere and at a temperature of 0° C. or 273° Kelvin) is normally in the gas phase, but under the conditions described may be in another phase. Thus the phrase "gas material" describes such substances as air, oxygen, nitrogen, carbon dioxide, etc., whether in the solid, liquid or gas phases.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

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

1. The process of removing impurities occurring in small amounts from gas material collected from a commercial source, which process comprises collecting in a substantial body the gas material including the impurity, said impurity occurring in said material at a concentration such that the boiling point of said gas material is not substantially changed thereby and having a melting point materially above the boiling point of said gas material, bringing said collected gas material substantially in the liquid phase into a heat exchanger in a condition in which the vapor pressure of said impurity has a substantially negligible value, heating the gas material in said exchanger in a manner such as to cause both liquid and gas phases to coexist therein without altering substantially the vapor pressure of said impurity, the said impurity then being contained wholly within the liquid phase of said material while the vapor pressure of said impurity is maintained at a substantially negligible value, and thereatfer withdrawing the vapors associated with said liquid phase and separating the same from said liquid phase whereby gas material free from said impurity is obtained.

2. The process of removing impurities occurring in small amounts from gas material collected from commercial sources which comprises collecting gas material which contains impurities both more volatile and less volatile than the gas material when liquefied, the impurities occurring in said gas material at concentrations such that the boiling point of said gas material is not substantially changed thereby, the less volatile impurity having a melting point materially above the boiling point of said gas material, bringing said collected material substantially in the liquid phase into a heat exchanger to a temperature and pressure corresponding substantially to a point on the liquid-gas phase equilibrium curve for said material, withdrawing the more volatile impurity while in a condition in which the vapor pressure of the less volatile impurity has a substantially negligible value, then heating the said material in a second stage so that both liquid and gas

phases co-exist, the less volatile impurity being contained wholly within the liquid phase of said material while the vapor pressure of said less volatile impurity remains substantially unaltered, and thereafter separating the gas phase associated with said liquid phase in said second stage whereby gas material free from said impurity may be withdrawn.

3. The process of removing impurities occurring in small amounts from gaseous mixtures obtained from the atmosphere in the commercial production of liquefied gases, which process comprises collecting a component of said gaseous mixture such as oxygen substantially in the liquid phase and containing the undesired impurity, said impurity occurring in said liquid oxygen at a concentration such that the boiling point of the liquid oxygen is not substantially changed thereby and having a melting point materially above the boiling point of liquid oxygen, bringing said liquid oxygen containing said impurity in a heat exchanger to a temperature and pressure corresponding substantially to a point on the liquid-gas phase equilibrium curve while in a condition in which the vapor pressure of said impurity has a substantially negligible value, adding heat to the introduced oxygen in a manner such that both liquid and gas phases coexist while said impurity is contained wholly within the liquid phase of the oxygen and the vapor pressure of said impurity remains substantially unaltered, and thereafter separating oxygen in the gas phase from the liquid phase whereby gaseous oxygen free from the undesired impurity is obtained.

LAWRENCE J. BOWDITCH.