Aug. 18, 1942. A. ETIENNE 2,293,601

PROCESS OF PRODUCTION OF MIXTURES OF GASES HARD TO LIQUEFY

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Fig. 1

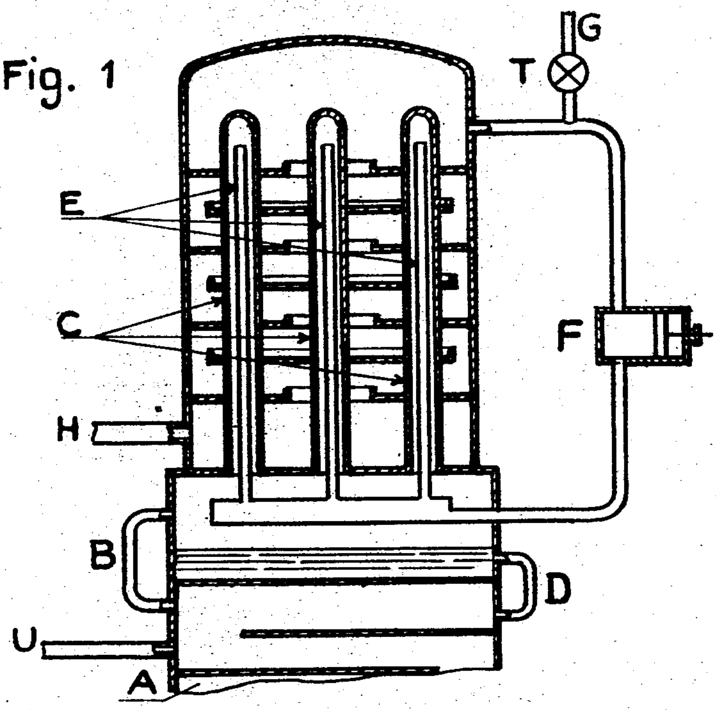
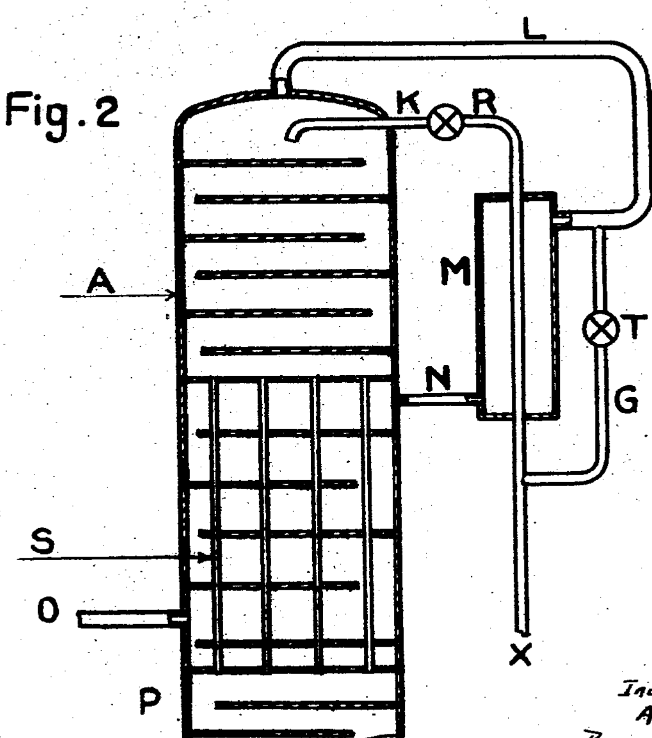


Fig. 2



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PROCESS OF PRODUCTION OF MIXTURES OF GASES HARD TO LIQUEFY

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This invention relates to the production of mixtures of difficultly-liquefiable gases, one of which at least is obtained by liquefying a gaseous mixture. One feature of the invention is that it is applicable to the production of nitrogen-hydrogen mixtures such as are to be utilized for ammonia synthesis and which must, as known, consist of one volume of nitrogen for three volumes of hydrogen. For the purpose of simplifying the following explanations, the production of such nitrogen-hydrogen mixtures will be referred to, but it is to be understood that the invention is also applicable inter alia to the production of mixtures of other liquefiable gases, such as carbon monoxide-hydrogen mixtures which, for instance, are to be utilized for the synthesis of organic compounds, as methyl alcohol.

In order to prepare, by partial liquefaction from coke oven or other similar gases, the nitrogen-hydrogen mixtures to be utilized for ammonia synthesis, it has been proposed to carry out the partial liquefaction of the coke oven gas and its final washing with liquid nitrogen under such temperature and pressure conditions that the obtained mixture, which consists of nitrogen and hydrogen, has the composition $N+H_3$, which is necessary for ammonia synthesis, but generally such temperature and pressure conditions cannot practically be made to prevail at the same time in economic manner, and the final gaseous mixture generally contains less than one volume of nitrogen for three volumes of hydrogen. In order to obtain a gaseous mixture having the composition $N+H_3$, the necessary make-up nitrogen is accordingly added to the final gaseous mixture. This addition of nitrogen is accompanied by no substantial thermal effect.

On the other hand, when obtaining mixtures of nitrogen and hydrogen, starting from coke oven gas, it has already been proposed to compress the coke oven gas, to cool it so as to separate therefrom, by liquefaction, the greater portion of the constituents other than hydrogen, to expand, with performance of external work, the gaseous effluent of the liquefaction, and to put the expanded gas into contact with liquid nitrogen. The liquid nitrogen vaporises in the expanded gas to give a resultant mixture of nitrogen and hydrogen. If the expanded gas is free from carbon monoxide, the liquid nitrogen is added in such a small quantity that it can wholly vaporise in the expanded gas. If, on the contrary, the expanded gas still contains carbon monoxide, the liquid nitrogen is added in greater quantity and the non-vaporised portion of the liquid nitrogen is utilized for washing the expanded gas so as to free it from its carbon monoxide. In both cases, if the obtained mixture of nitrogen and hydrogen contains less than one volume of nitrogen for three volumes of hydrogen, which will generally be the case, there must be subsequently added thereto the quantity of nitrogen in gaseous state which is necessary for obtaining a mixture of hydrogen and nitrogen suitable for ammonia synthesis.

In the process according to this invention, the hydrogen (or more generally a first difficultly-liquefiable gas resulting from the separation of a gaseous mixture by liquefaction) is admixed with nitrogen (or a second gas hard to liquefy), namely under such conditions that a useful thermal effect is brought about.

The process according to the present invention for producing mixtures of difficultly-liquefiable gases consists in cooling a gaseous mixture, liquefying it so as to separate therefrom a first gas which is to become a constituent of the gaseous mixture to be produced, cooling a second gas which is also to become a constituent of the gaseous mixture to be produced, mixing the less volatile of these two constituents, in the liquid state, with the other constituent in the gaseous state, the constituent in the liquid state being at a temperature sufficiently low and being of sufficiently great quantity, that at least a portion of said liquid constituent does not vaporise when the addition takes place, and maintaining the mixture of gas and liquid thus constituted in heat exchange relation to the gases to be cooled, for instance, the treated gaseous mixture, so that there is an exchange of heat from the gases to be cooled to the liquid and gaseous mixture, such exchange of heat taking place either at the end of the purification of the gaseous mixture during the course of its treatment.

When applied to the production of nitrogen-hydrogen mixtures of the kind referred to above, the process consists in cooling the gaseous nitrogen, liquefying it and admixing it while in its liquid state with gaseous hydrogen, the liquid nitrogen being at so low a temperature and in so great a quantity that at least a portion of the liquid nitrogen does not vaporise at the time of the addition. The mixture of gas and liquid thus constituted is then warmed up, its cold being transferred to the gases to be cooled. During this warming up, the liquid nitrogen (or more generally the less volatile of the two constituents of the mixture to be produced) vaporises progressively while imparting to the gas-liquid mixture, of which it is a part, the temperature which corresponds to the partial pressure of the nitrogen in the gaseous phase, which temperature constantly remains lower than the temperature which the nitrogen (or the less volatile gas) would have if it would vaporise alone under the pressure of the mixture. By thus vaporising the liquid nitrogen in the hydrogen it is possible to obtain the favorable effect of a lowering of temperature in the colder region of the separating apparatus.

From the place where the liquid nitrogen and the gaseous hydrogen (or the gas and the liquid) are mixed, no further purification of the mixture by partial condensation can take place. Therefore, it is important that the formed mixture be free from obnoxious impurities. Thus, if one is concerned with the production of a $N+H_3$ mixture substantially free from carbon monoxide, it will generally be necessary to wash, in known manner, with liquid nitrogen the gaseous effluent of the partial liquefaction of the coke oven gas before adding thereto the make-up nitrogen in the liquid state.

The process of the invention will be described hereinafter by way of example in the special case above referred to, that is, where one is concerned with producing from coke oven gas a mixture of nitrogen and hydrogen of the composition $N+H_3$. For this description, reference will be made to the accompanying drawing which diagrammatically shows, in elevation, two forms of apparatus in which the final cooling of the gaseous mixture subjected to liquefaction takes place. Fig. 1 relates to the case where an expanded mixture of $N+H_3$ is withdrawn from the apparatus, and Fig. 2 to the case where such a mixture is still under the initial pressure to which the coke oven gas has been compressed.

In Fig. 1, coke oven gas, which has previously been cooled in heat exchangers, not shown, and stripped by partial liquefaction of its ethylene, the greater part of its methane, and possibly of a portion of its carbon monoxide, rises through the washing column A, in which it is washed by pure liquid nitrogen. The substantially pure mixture of nitrogen and hydrogen obtained at the top of the column A passes through the pipe B to a nest of tubes C, closed at their upper end. These tubes are cooled externally, in a manner which will be described later, to such an extent that nitrogen condenses therein. It is this liquid nitrogen which is conveyed through the pipe D to the top of the washing column A. From the top of the closed tubes C, the nitrogen-hydrogen mixture flows downward through the open-ended tubes E located inside the tubes C and is warmed by indirect contact with the gas rising in the tubes C. From the lower end of the tubes E, the nitrogen-hydrogen mixture is passed to an expansion engine F, in which it expands with production of external work, and with resultant lowering of its temperature. Liquid nitrogen under pressure is conveyed through the pipe G, expanded through the valve T to the pressure of the expanded hydrogen-nitrogen mixture and added thereto. The liquid nitrogen introduced through the pipe G previously has been cooled to a low temperature by heat exchange with the products resulting from the separation of coke oven gas into its constituents, and is in such quantity that the mixture resulting from its union with the expanded mixture of hydrogen and nitrogen has substantially the composition of $N+H_3$. Under these conditions, the liquid nitrogen introduced through the pipe G is in quantity sufficiently great and at a temperature sufficiently low that at least a portion thereof remains in the liquid state in the gaseous mixture to which it is added. It is the resulting mixture of liquid nitrogen and of gas from the expansion engine F which flows around the external tubes C while subjecting them to the above mentioned cooling. After having been warmed up by contact with these tubes, the mixture passes out through the pipe H.

In certain cases it may happen that the amount of liquid nitrogen condensed in the pipes C is too small to accomplish a satisfactory washing of the coke-oven gases in the column A. In such cases supplementary liquid nitrogen will then be introduced into the column A through the pipe U at the top thereof.

In Fig. 2, the compressed coke oven gas, which has previously been cooled under the same conditions as in the case of Fig. 1, and which still contains an important proportion of carbon monoxide, flows upwardly successively through a washing column P, a nest of tubes S and a second washing column A. In the column P, the compressed gas is washed with liquid nitrogen still containing some carbon monoxide and is stripped only incompletely of its carbon monoxide, in the nest of tubes S it is cooled as will be mentioned hereinafter. Such cooling of the compressed gas in the tubes S brings about a partial condensation of the gas. In the washing column A the uncondensed gas is washed with pure liquid nitrogen, conveyed to the column through the pipe K, which takes up in known manner the small quantities of carbon monoxide which remain in the gaseous mixture. The liquid nitrogen flows downwardly successively through the column A, the nest of tubes S and the column P, thereby growing richer in carbon monoxide. On the other hand, in an apparatus not shown, nitrogen is compressed and brought to a low temperature in liquid state by being put in heat exchange with the products resulting from the separation of the coke oven gas into its constituents. The cold liquid nitrogen thus obtained enters the pipe X and is divided into two parts. One part passes through the exchanger M where it is cooled, and is expanded through the valve R and constitutes the aforementioned washing liquid nitrogen which is introduced to the upper end of column A through the pipe K. The other part passes through the pipe G, is expanded through the valve T and is added to the substantially pure hydrogen-nitrogen mixture which results from the washing operation carried out in the column A, and which leaves through the pipe L. This second portion of liquid nitrogen is in such quantity that the obtained mixture of gas and liquid has substantially the composition $N+H_3$. The mixture of liquid and gas thus formed flows through the exchanger M, in which it cools the liquid nitrogen delivered at the top of the column A through the pipe K. When leaving the exchanger M, the nitrogen-hydrogen mixture, still containing some liquid and still under pressure, is passed through the pipe N around the nest of tubes S, where it cools the gaseous mixture rising through said tubes, and leaves through the pipe O after being wholly or partially vaporized.

A portion of the nitrogen contained in the gaseous mixture rising through the nest of tubes S liquefies and unites with the liquid nitrogen descending from the column A. The production of cold is obtained, for instance, by means of a nitrogen cycle.

In the example of Fig. 2, the cooling of the liquid nitrogen in the exchanger M could in certain cases be suppressed.

The liquid mixture of carbon monoxide and nitrogen resulting from the separation of the coke oven gas into its constituents is preferably utilized as the medium for the cooling of the compressed nitrogen which is to constitute the make-up liquid nitrogen in the two examples given above. But the gaseous mixture of hydrogen and nitrogen obtained as the other product of the separation of the coke oven gas into its constituents could also be so utilized. In that case, the mixture of hydrogen and nitrogen will preferably be partly warmed before being utilized for cooling the nitrogen. As to the preliminary cooling of the nitrogen, it is obtained either by putting compressed nitrogen in heat exchange with the separation products and especially the liquid methane, or by directly expanding the compressed nitrogen, at the surrounding temperature, or after being partially cooled, to an intermediate pressure which permits its liquefaction by heat exchange with the cold separation products.

The origin of the make-up nitrogen utilized in the liquid state in the two above examples is immaterial. The nitrogen can, for example, be obtained by rectifying the liquid mixture of nitrogen and carbon monoxide obtained by cooling and washing the coke oven gas, and warming up the gaseous nitrogen resulting from this rectification in order to compress it at the surrounding temperature.

It has been assumed in the foregoing that the starting gaseous mixture is coke oven gas, but the process would still be applicable, unaltered, if the starting gas were water-gas or any other similar hydrogen-containing gaseous mixture. Again, the process according to the invention may be applied to the obtention of hydrogen-carbon monoxide mixtures by partial liquefaction of hydrogen-containing gaseous mixtures. In that case the washing of the gas with liquid nitrogen will, of course, be dispensed with and there will be obtained a gaseous mixture consisting of hydrogen and a little carbon monoxide and nitrogen, to which carbon monoxide will be added in the liquid state. More generally, the process is applicable to the production of mixtures of difficultly-liquefiable gases, one of which at least is obtained by the separation of a gaseous mixture by liquefaction.

I claim:

1. A process for producing mixtures of difficultly-liquefiable gases containing a constituent of greater volatility and a constituent of less volatility which comprises cooling a gaseous mixture containing the constituent of greater volatility sufficiently to separate said constituent from other constituents of the gaseous mixture by liquefaction, mixing said separated constituent, in the gaseous state, with the constituent of less volatility, in the liquid state, the constituent of less volatility being in an amount sufficiently great and at a temperature sufficiently low that at least a portion thereof is not vaporized when added to the more volatile constituent in the gaseous state, and passing the resultant mixture of gas and liquid into heat exchange relation with the first-mentioned gaseous mixture to cool said first-mentioned gaseous mixture and to cause the liquid of the liquid-and-gas mixture to be vaporized.

2. A process for the production of difficultly-liquefiable gases as set forth in claim 1, in which the heat exchange between the resulting mixture of gas and liquid and the first-mentioned gaseous mixture takes place at the end of the cooling of the first-mentioned gaseous mixture to separate the constituent of less volatility.

3. A process for the production of difficultly-liquefiable gases as set forth in claim 1, in which the heat exchange between the resulting mixture of gas and liquid and the first-mentioned gaseous mixture takes place at an intermediate stage of the cooling of the first-mentioned gaseous mixture to separate the constituent of less volatility.

4. A process for producing mixtures of hydrogen and nitrogen having the composition $N+H_3$ which comprises washing a gaseous mixture containing hydrogen with liquid nitrogen, mixing the resulting gaseous mixture containing hydrogen and nitrogen, in the gaseous state, with liquid nitrogen, the amount of admixed liquid nitrogen being sufficiently great and its temperature sufficiently low that at least a portion thereof is not vaporized when added to the gaseous mixture containing hydrogen and nitrogen, and passing the resulting mixture of gas and liquid into heat exchange relation with the gaseous mixture resulting from the washing of the first-mentioned gaseous mixture with liquid nitrogen to cool it and to cause the liquid of said liquid-and-gas mixture to be vaporized.

5. A process for producing mixtures of hydrogen and nitrogen having the composition $N+H_3$ which comprises washing a gaseous mixture containing hydrogen with liquid nitrogen, subjecting the resulting gaseous mixture containing hydrogen and nitrogen to cooling sufficient to liquefy at least part of the nitrogen thereof, mixing the remainder of the mixture, in the gaseous state, with liquid nitrogen, the amount of admixed liquid nitrogen being sufficiently great and its temperature sufficiently low that at least a portion thereof is not vaporized when added to said remainder of the mixture, and passing the resulting mixture of gas and liquid into heat exchange relation with the gaseous mixture resulting from the washing of the first-mentioned gaseous mixture with liquid nitrogen to cool it and to cause the liquid of said liquid-and-gas mixture to be vaporized.

6. A process for producing mixtures of hydrogen and nitrogen having the composition $N+H_3$ which comprises washing a gaseous mixture containing hydrogen with liquid nitrogen, mixing the resulting gaseous mixture containing hydrogen and nitrogen, in the gaseous state, with liquid nitrogen, the amount of admixed liquid nitrogen being sufficiently great and its temperature sufficiently low that at least a portion thereof is not vaporized when added to the gaseous mixture containing hydrogen and nitrogen, and passing the resulting mixture of gas and liquid into heat exchange relation with the first-mentioned gaseous mixture while it is being washed with the liquid nitrogen to cool said first-mentioned gaseous mixture and to cause the liquid of said liquid-and-gas mixture to be vaporized.

7. A process for the production of mixtures of hydrogen and nitrogen as set forth in claim 4, in which the liquid nitrogen used for washing the first-mentioned gaseous mixture is cooled by heat exchange with said liquid-and-gas mixture.

8. A process for producing a mixture of low-

boiling gases which comprises partially liquefying a mixture of low-boiling gases by cooling said mixture to a low temperature, adding a liquefied low-boiling gas to the gaseous effluent of said partial liquefaction, the liquefied low-boiling gas being in an amount sufficiently great and at a temperature sufficiently low that at least a portion thereof is not vaporized when added to the gaseous effluent of said partial liquefaction, and passing the resultant mixture of gas and liquid into heat exchange relation with the mixture of gases to be partially liquefied.

9. A process for producing a mixture of hydrogen and nitrogen which comprises cooling a hydrogen-containing gaseous mixture sufficiently to partially liquefy it, washing the non-liquid portion of said gaseous mixture with liquid nitrogen, mixing the gases resulting from said washing operation with a further quantity of liquid nitrogen, said further quantity of liquid nitrogen being in an amount sufficiently great and at a temperature sufficiently low that at least a portion thereof is not vaporized when added to the gases from said washing operation, and passing the resultant mixture of gas and liquid into heat exchange relation with the gases to be partially liquefied.

10. A process for producing a mixture of hydrogen and nitrogen which comprises cooling a hydrogen-containing gaseous mixture sufficiently to partially liquefy it, washing the non-liquid portion of said gaseous mixture with liquid nitrogen, mixing the gases resulting from said washing operation with a further quantity of liquid nitrogen, said further quantity of liquid nitrogen being in an amount sufficiently great and at a temperature sufficiently low that at least a portion thereof is not vaporized when added to the gases from said washing operation, and passing the resultant mixture of gas and liquid into heat exchange relation to the non-liquid portion of the gases resulting from the partial liquefaction of the hydrogen-containing gaseous mixture while said non-liquid portion is being subjected to the washing with liquid nitrogen.

11. A process for producing a mixture of hydrogen and nitrogen which comprises cooling a hydrogen-containing gaseous mixture sufficiently to partially liquefy it, washing the non-liquid portion of said gaseous mixture with liquid nitrogen, further cooling the washed gases, expanding said washed gases with external work, mixing the expanded gases with liquid nitrogen, said last-mentioned liquid nitrogen being in an amount sufficiently great and at a temperature sufficiently low that at least a portion thereof is not vaporized when it is added to the expanded gases, and passing the resulting mixture of gas and liquid into heat exchange relation with the washed gases which are to be further cooled.

12. A process for producing a mixture of hydrogen and nitrogen which comprises cooling a hydrogen-containing gaseous mixture sufficiently to partially liquefy it, washing the non-liquid portion of said gaseous mixture with liquid nitrogen, mixing the gases resulting from said washing operation with a further quantity of liquid nitrogen, said further quantity of liquid nitrogen being in an amount sufficiently great and at a temperature sufficiently low that at least a portion thereof is not vaporized when added to the gases from said washing operation, and passing the resultant mixture of gas and liquid into heat exchange relation first with said washing liquid nitrogen and then with the non-liquefied portion of the hydrogen-containing gaseous mixture while said non-liquid portion is being subjected to the washing with liquid nitrogen.

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