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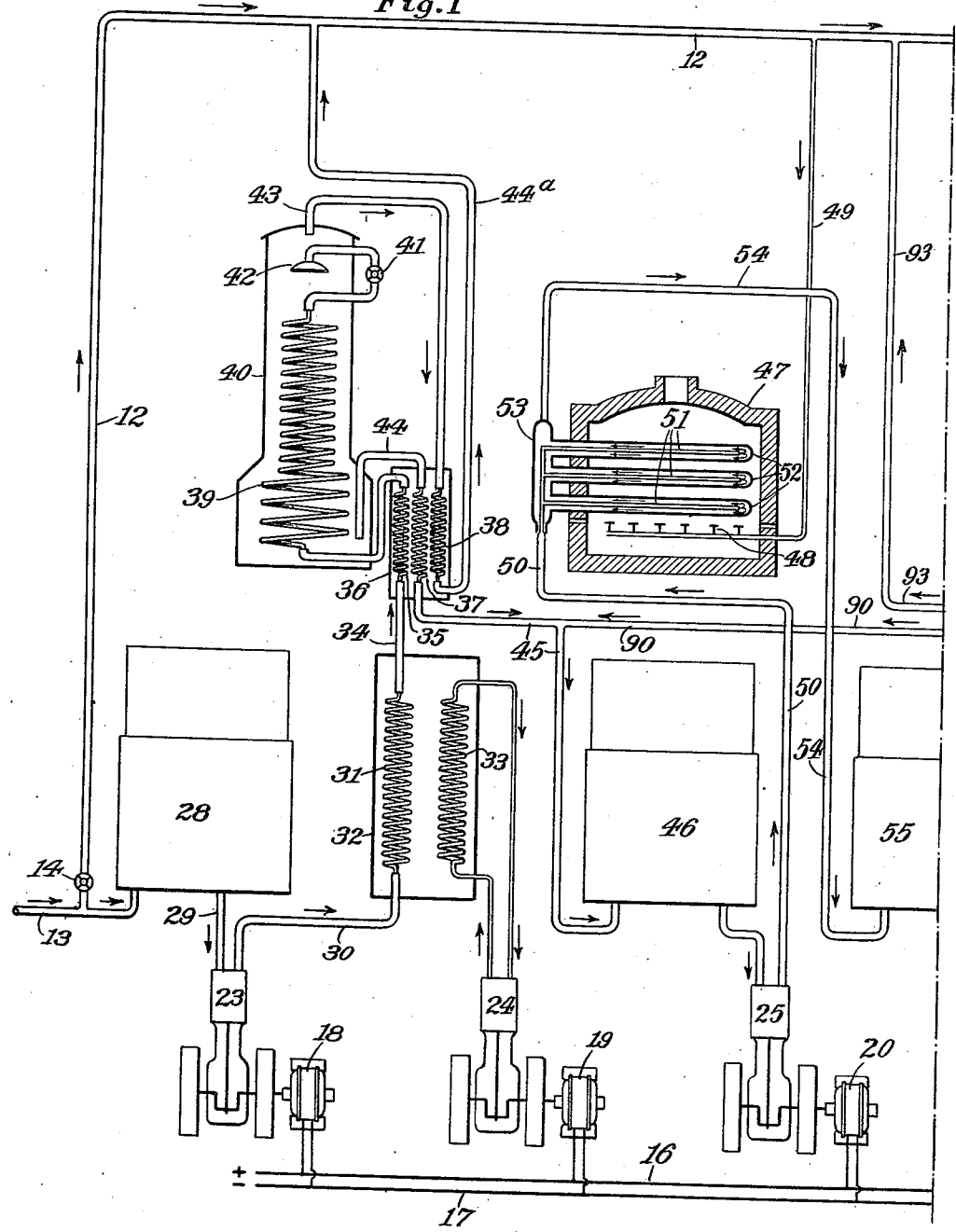
P. E. HAYNES ET AL
PRODUCTION OF ETHYLENE

1,460,545

Filed March 9, 1918

2 Sheets-Sheet 1

Fig. 1



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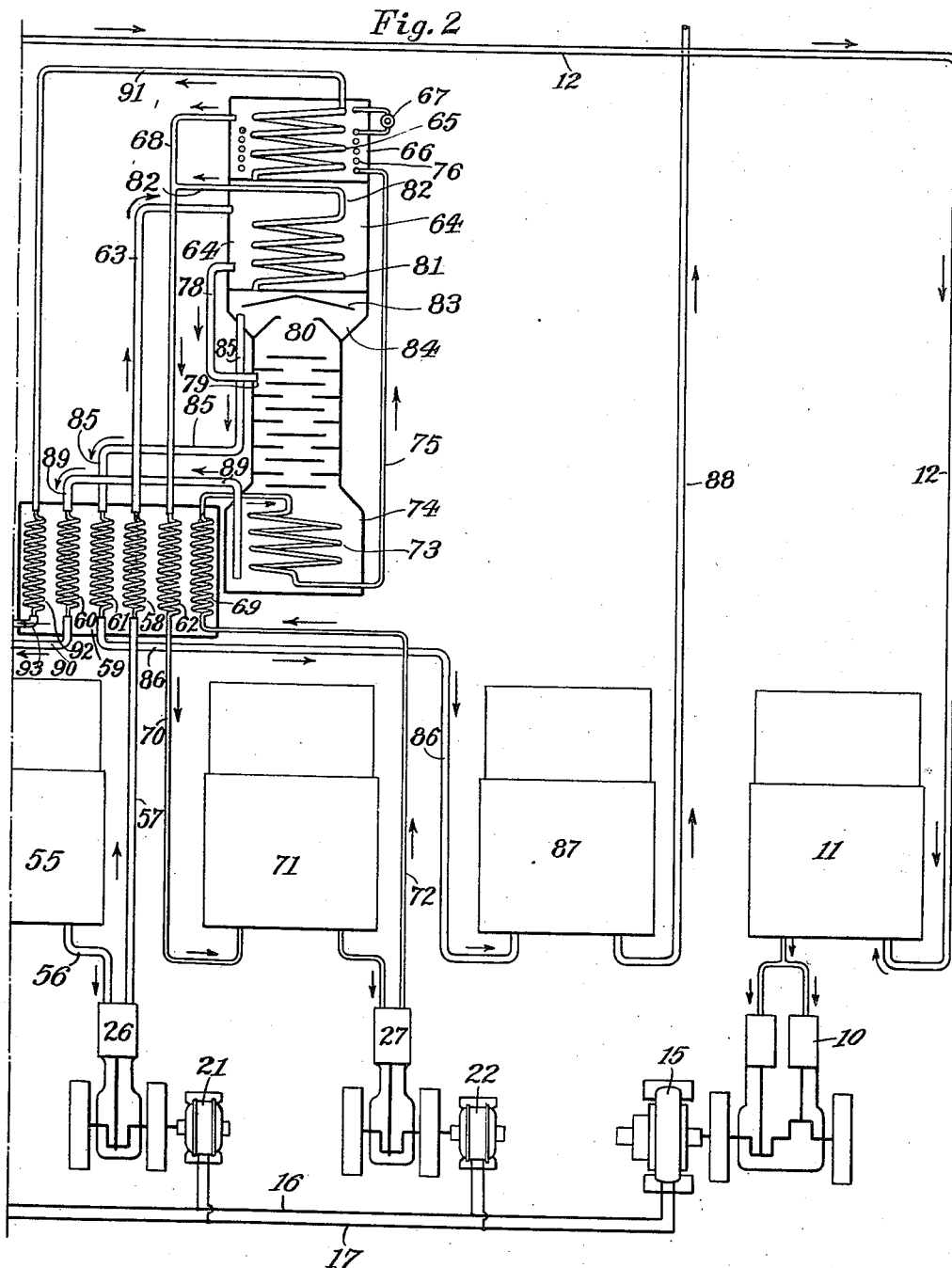
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INVENTORS
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UNITED STATES PATENT OFFICE.

PIERRE E. HAYNES, OF BUFFALO, NEW YORK, AND GEORGE O. CURME, JR., OF PITTSBURGH, PENNSYLVANIA, ASSIGNORS TO THE LINDE AIR PRODUCTS COMPANY, OF CLEVELAND, OHIO, A CORPORATION OF OHIO.

PRODUCTION OF ETHYLENE.

Application filed March 9, 1918. Serial No. 221,407.

To all whom it may concern:

Be it known that we, PIERRE E. HAYNES and GEORGE O. CURME, Jr., both citizens of the United States, residing, respectively, at Buffalo, county of Erie, and State of New York, and at Pittsburgh, county of Allegheny, and State of Pennsylvania, have invented certain new and useful Improvements in the Production of Ethylene, of which the following is a full, clear, and exact description.

This invention relates to the manufacture of ethylene and its chief object is to provide a simple and effective process or method by which the compound can be produced in a high degree of purity from initially impure ethane, as for example ethane contained in natural gas. A further object is to provide a continuous process for obtaining ethane and from the latter, ethylene. To these and other ends the invention consists in the novel method hereinafter described.

Suitable and convenient apparatus for carrying out our invention in the preferred manner is illustrated diagrammatically in the accompanying drawing, in which—

Fig. 1 shows the first half and Fig. 2 the second half of the apparatus.

The ethane required can be obtained from any source containing the same, as for example natural gas.

When natural gas is the raw material used, the substances associated with the ethane should be removed. Such substances include water, carbon dioxide, hydrogen sulfide, benzol, toluol, propane, butane, hexane, etc. Methods and apparatus for removing such impurities are well known and hence need not be described herein. Methane and other substances boiling at lower temperatures than ethane should also be removed and the manner of effecting this separation will now be described. When other gas mixtures are taken as raw material, the ethane should first be isolated as in the case of natural gas.

In the particular apparatus illustrated the energy required for the various steps of the process is derived from the natural gas from which ethylene is to be produced. For this purpose an internal combustion engine 10 is provided, supplied with gas from a fuel-gas holder or gasometer 11 which is itself connected by a pipe 12 with the source of

natural gas represented by the pipe 13. As will be seen hereinafter, unmodified natural gas is only a part of the fuel by which the engine is driven. To regulate the amount of unmodified gas delivered to the holder the pipe 12 is provided with a fuel-make-up valve 14. The engine 10 drives an electric generator 15, connected by leads 16, 17 to motors 18, 19, 20, 21, 22, which drive the compressors 23, 24, 25, 26, 27, respectively.

A suitable supply of natural gas from the pipe 13 is accumulated and maintained in the gasometer 28, whence it is withdrawn through pipe 29 and compressed by the natural gas compressor 23. Compressor 23 and pipe 30 may be provided with suitable drains (not shown) for the removal of any constituents (of the gas) that may be condensed at this stage. From the compressor the gas is delivered through the pipe 30 to coil 31 of a suitable pre-cooler 32, which is cooled by a suitable refrigerant, such as ammonia or carbon dioxide, driven through coil 33 by compressor 24. The coil 31 is preferably provided with a drain (not shown) for the withdrawal of any substances condensing at this stage, as for instance water, hexane, pentane, butane, propane, benzol, toluol, etc. A duplicate pre-cooler, not shown, may be provided, for use in case the other should be clogged or choked by freezing.

The compressed and pre-cooled gas is now ready for the concentration of its ethane or such part of its ethane as may be needed for the purpose in hand. This concentration is in the present process effected by liquefaction, and is attained by the continuous expansion of the gaseous mixture (in the present instance natural gas or a mixture derived therefrom) within the liquefier from a high to a low pressure. Conservation of "cold" is secured by means of a heat exchanger in which the mixture, (now separated into liquefied ethane plus liquefied constituents of the natural gas which have higher boiling points than ethane), and a gaseous portion of the other constituents, are passed back, thus absorbing heat from the incoming compressed gas, which latter is advancing toward the expansion orifice or valve. In this way it is possible to economically liquefy ethane in a mixture of ethane, methane, and other gases of lower boiling points, by adjust-

ment of the ratio of the pressure of the unexpanded to the pressure of the expanded gas, as will be readily understood by those skilled in the art.

5 For the purpose of subjecting it to the treatment or step outlined above, the compressed and precooled gas is delivered through pipe 34 to coil 35 of the heat-exchanger 36. Here the gas is further cooled, 10 by cold gases flowing counter-current in the coils 37, 38, and then passes into coil 39 of the ethane liquefier and separator 40, where the gas gives up still more heat, this time to the liquid (ethane and perhaps other 15 gases) in which said coil, or at least the lower portion thereof, is immersed. Passing through coil 39 the cooled gas issues from the expansion valve 41. By adjustment of the ratio of the pressure of the unexpanded to the pressure of the expanded 20 gas a temperature is reached, by virtue of the expansion, at which ethane is liquefied, thus causing a separation of the emergent mixture into a liquid portion containing 25 practically all the ethane, and a gaseous portion containing lower boiling constituents which do not liquefy at the temperature produced by the expansion. From the spray head 42 the uncondensed or gaseous portion 30 passes through pipe 43 to coil 38 of the heat-exchanger 36, where as already explained, it assists in cooling down the high-pressure gas from the pre-cooler 32. The aforesaid liquid portion, consisting chiefly of ethane, 35 flows down over coil 39 and by absorption takes heat from the incoming high-pressure gas, which absorption serves by evaporation or rectification to remove any remaining traces of constituents boiling at tempera- 40 ture lower than the boiling point of ethane. Practically pure ethane in liquid form thus collects in the bottom of the separator chamber, whence it is delivered by pipe 44 to coil 37 of heat-exchanger 36. Here the liquid 45 is warmed and evaporated by the high-pressure gas flowing through coil 35. The gases emerging from coils 37 and 38 are still at a temperature below that of the surrounding atmosphere, and if desired may be 50 passed (by suitable apparatus, not shown) in heat-exchanging relation to the high-pressure gas in pipe 30 before such gas reaches the pre-cooler 32. Otherwise the gas from coil 38 is delivered by way of pipe 55 44^a to the fuel-gas line 12 where it mingles with the natural gas flowing from pipe 13 to the gasometer 11, while the gas (practically pure ethane) from coil 37 passes by way of pipe 45, to the ethane gasometer 46 60 for storage.

The ethane or a mixture rich in ethane, obtained and isolated as above described, is now ready for treatment to produce ethylene. This is essentially a heat treatment, 65 and is based upon the known fact that

ethane is decomposed at high temperatures into ethylene and hydrogen according to the equation $C_2H_6=C_2H_4+H_2$. When the temperature is reduced the reaction proceeds 70 in the direction of ethane formation, and in the direction of ethylene and hydrogen formation when the temperature is increased. It is also known that the equilibrium concentrations of the various gases involved 75 are approximately constant at a given temperature and vary with change in temperature. Hence by proper choice of temperature and pressure conditions, and by using a suitable reaction vessel, the decomposition 80 can be effected so as to give approximately the theoretical yield of ethylene and hydrogen. We prefer to treat the ethane at a temperature exceeding 500° C. Above 685° 85 or thereabouts the ethylene formed may be decomposed to a slight extent, and such decomposition is greater at higher temperatures. Hence the temperature should not 90 be higher than about 900°. It has also been found that the ethylene formed may be decomposed if subjected to heat at the higher temperatures for too long a time. In 95 general, the period of treatment should vary inversely as the temperature change. The most favorable pressure we have found to be slightly in excess of atmospheric. The 100 material of the containing walls with which the gases come in contact during the heat treatment is important in that it should have no injurious catalytic effect on the ethylene formed. Thus when certain metals, 105 such as iron, nickel, or platinum, are used, an effect is observed which results in partial destruction of the ethylene. We find, however, that copper, porcelain and the common vitreous materials, do not have the property 110 of acting injuriously at the temperatures named. The method of heating the ethane is not, in general, important, but in the present process the availability of a combustible gaseous by-product makes the latter 115 a convenient source of heat. It is recognized, however, that some advantage is to be had in electrically heated reaction tubes on account of the ease afforded for temperature control, and the possibility of more thorough heat insulation.

For carrying out the above step of our process a furnace 47 is provided, heated by gas burners 48 supplied by a small pipe 49 120 leading from the fuel-gas line 12. From the ethane gasometer 46 the gaseous ethane is withdrawn by the compressor 25 and delivered through pipe 50 to the inner pipes 51 inside the furnace 47. The pipes 51 are 125 connected "in parallel" to pipe 50 and are enclosed by the outer or return pipes 52 which are connected to the heat-exchanger 53 so that the incoming ethane, which is relatively cool, can absorb heat from the outgoing hot ethylene. In accordance with 130

what we have said in the preceding paragraph, the heating pipes or reaction chambers, and any other parts with which hot ethylene may come in contact, are composed of or surfaced with an inert material, preferably copper.

From the heat-exchanger 53 the ethylene is led by way of pipe 54 to the crude ethylene gasometer 55.

The ethane-conversion product or reaction product obtained in the above manner is rich in ethylene, mixed with hydrogen, methane, unchanged ethane, and possibly other impurities. Any carbon, tar, or like substances present can be removed by any convenient method, not shown.

To isolate the ethylene the gaseous mixture containing the same is taken from gasometer 55 by pipe 56 to compressor 26, by which it is compressed. Passing through pipe 57 to coil 58 of heat-exchanger 59 the compressed gas is cooled by cold gases flowing counter current in coils 60, 61, 62, 92, as hereafter described. From coil 58 the cooled mixture flows through pipe 63 to vessel 64 and thence passes into condenser 65, which is partly immersed in a refrigerating bath, preferably liquid methane, contained in vessel 66. The liquid methane is obtained by the expansion of previously cooled high-pressure methane at the expansion valve 67. The methane evaporated in vessel 66 passes therefrom by way of pipe 68 to coil 62 of heat-exchanger 59 where it serves to cool down the previously compressed warm gases flowing counter-current in coils 58 and 69. Thence the methane, now warmed, goes through pipe 70 to the methane storage gasometer 71. From the latter it is drawn by compressor 27 and is delivered to the pipe 72 leading to the aforesaid coil 69 of the heat-exchanger. In this coil the gas gives up heat to the cold gases flowing counter-current in coils 60, 61, 62 and 92, and passes then to coil 73 which is immersed in liquefied ethane and ethylene in the vessel 74. This mixture of liquefied ethane and ethylene is boiled by the high-pressure methane, and the latter is reciprocally cooled by the heat-exchange. From coil 73 the methane passes through pipe 75 to coil 76, which is immersed in the liquefied methane, previously mentioned, in vessel 66. Here the high-pressure methane receives its final cooling before reaching the expansion valve 67, which is connected to the aforesaid coil 76. The refrigerating agent (methane) thus flows continuously through a closed circuit, in which it is continuously liquefied and evaporated alternately.

The gaseous mixture (or crude ethylene) delivered to vessel 64 by pipe 63, as stated above, rises into the condenser 65 and is there cooled. Ethane, ethylene, and more or

less methane (if any of the latter be present in the mixture) are condensed and run back into vessel 64, while hydrogen and the rest of the methane pass on through the condenser and are delivered to pipe 91. The gases (ethane, ethylene and methane) condensed in the condenser 65 collect in vessel 64 and thence pass through pipe 78 and are delivered to a suitable point in the rectifying tower or column 79 between vessels 74 and 84. The more easily evaporated constituents (ethylene and methane) of the liquefied mixture pass up the tower in gaseous form and through the opening 80 into the condenser 81 in vessel 64, cooled by the ethane, ethylene and methane liquefied in the condenser 65 as explained above. In the condenser 65 the said ethane, ethylene and methane are not only liquefied but are also supercooled, and it is therefore possible to maintain the liquid (in vessel 64) at a temperature considerably below the boiling points of ethane and ethylene, thus cooling the condenser 81 to a point insuring condensation of the ethylene rising therein from the tower 79; but at the same time the pressure in the tower 79 is kept at such point that the methane rising therefrom will not be condensed in coil 81 and will therefore pass on through pipe 82 to pipe 68 leading to coil 62 of the heat exchanger 59. Thus the methane coming into vessel 64 as an impurity in the crude ethylene is added to the methane which is used as a refrigerating agent to cool, the condenser 65. The condensable constituents of the gaseous mixture rising into coil 81 drop down upon the baffle trough or vessel 84 at the top of the rectifying tower. The liquid thus collected overflows into the opening 80, thereby washing or lixiviating the gases rising in the tower. These gases, being evaporated from the liquefied crude ethylene delivered by pipe 78, and being therefore chiefly ethylene, pass on and up into the condenser coil 81 and there the ethylene is condensed while the gaseous methane content escapes by way of pipe 82 as already described. The gaseous ethane content is absorbed or liquefied by the lixiviating liquid and runs back into vessel 74 at the bottom of the tower where it adds itself to the liquid ethane in which coil 73 is immersed. As the operation continues, less and less gas of higher boiling point than ethylene escapes from the rectifying tower through opening 80, until eventually none or practically none escapes at all and the liquid condensed in condenser 81 and collected in vessel 84 is then pure or substantially pure ethylene. At the same time practically all the liquid ethylene overflowing into the rectifying tower and evaporating therein is recondensed in the condenser

81 and is added to the pure ethylene in vessel 84. From the latter, ethylene is withdrawn continuously by pipe 85 and passed through coil 61 of the heat-exchanger 59 where it absorbs heat from the relatively warm gases in coils 58 and 69 and then passes on through pipe 86 to the pure ethylene gasometer 87. From the latter the gas is withdrawn as needed through pipe 88.

The ethane delivered to the rectifying tower 79 collects in vessel 74, usually with some ethylene, and is withdrawn by pipe 89 through coil 60 of heat-exchanger 59, where it absorbs heat from the warmer gases in coils 58 and 69, and passes thence through pipe 90 to pipe 45 where it mingles with ethane from the liquefier 40 and goes onto the ethane storage gasometer 46, from which, as before described, ethane is delivered to the reaction chambers in furnace 47.

The uncondensable gases (chiefly if not entirely methane and hydrogen) delivered to the condenser 65 are discharged through pipe 91 and conducted to coil 92 of the heat exchanger 59, where they serve to cool the relatively warm gases flowing counter-current in coils 58 and 69, and are led thence by pipe 93 to the fuel-gas line 12. Through

the latter pipe they pass with the other gases therein to the storage gasometer 11.

It is to be understood that the invention is not limited to the specific apparatus and procedure herein specifically described but can be carried out in other ways without departure from its spirit. For example, the preferred procedure is, as is seen from the foregoing description, continuous, but we do not limit ourselves to a continuous method.

We claim:

1. A process of forming ethylene from gaseous hydrocarbon mixtures containing ethane, which comprises the steps of isolating ethane from the mixture in a state of substantial purity and heat treating the ethane under substantially optimum conditions for the production of ethylene.

2. Process according to claim 1, wherein ethylene and residual ethane are isolated from the product of the heat-treatment, and the ethane is returned to the cycle at a point preceding the heat-treatment.

In testimony whereof we hereunto affix our signatures.

PIERRE E. HAYNES.
GEORGE O. CURME, JR.