[Second Edition.]

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to Methyl Ether.

We, DELCO-LIGHT COMPANY, incorporated under the laws of the State of Delaware, United States of America, of Dayton, Ohio, United States of America, Assignees of FRANCIS RUSSELL BICHOWSKY, a citizen of the United States of America, of 2904, P. Street, S.E., Washington, D.C., United States of America, formerly of 316, Rossiter Avenue, Baltimore, Maryland, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture and recovery of methyl ether and in one of its aspects has reference to the production of methyl ether by passing methyl alcohol over dehydrating catalysts at temperatures of about 300° C.

The present invention according to one of its aspects may be said to consist in producing methyl ether by the process above referred to under pressure.

In the production of methyl alcohol it is known to combine carbon monoxide with hydrogen at elevated temperatures and pressure in the presence of certain catalysts and according to a further aspect the present invention includes the production of methyl alcohol in situ by the said process.

The single figure of the annexed drawing shows one form of apparatus suitable for the process.

We have found that methyl ether can be made very cheaply by passing carbon monoxide and hydrogen, over a hydrogenation catalyst and a dehydrating catalyst at high temperatures and pressures. The two separate catalysts we call catalyst (A) and catalyst (B). The first of these (A) should be a hydrogenation catalyst which does not favor the formation of methane. There are several such substances or mixtures of substances which will give satisfactory results, among which may be mentioned zinc oxide and reduced salts of copper or chromium. The second (B) is a dehydrating catalyst, such as hydrous aluminium oxide prepared by partially dehydrating aluminium hydroxide at a temperature of about 300° C. or partially dehydrated titanium oxide, thorium oxide or silica gel. The carbon monoxide and hydrogen should be brought in contact with the hydrogenation catalyst at a temperature of about 500° C. and under a pressure of the order of 125 atmospheres or more, and should be brought in contact with the dehydrating catalyst at a temperature of about 300° C. and a pressure of 25 atmospheres or more.

The process may be carried out as follows:

A furnace 10 is charged or packed with the catalyst. We may place the hydrogenation catalyst in the front part 11 of the furnace and the dehydrating catalyst in the rear part 12. The furnace is then heated to a high temperature, by which we mean 300° C. or more. We prefer to heat the front portion to a higher temperature than the back portion, namely, to about 500° C. In practice, this may be accomplished conveniently merely by heating the front portion to 500° C. by any suitable source of heat, conventionally indicated as a burner 13.

Carbon monoxide and hydrogen, in the proportion of two or more parts by volume of hydrogen to one of carbon monoxide are passed into the furnace at 14 under high pressure. In this part of the process, we mean 125 atmospheres or more, we find that 150 atmospheres is a good operating pressure.

Methyl ether and water result from the catalytic action and come off at 16, the following reaction occurring within the furnace:

$$2CO + 4H_2 = CH_3OCH_3 + H_2O$$

It is essential that this process be carried out in the absence of iron, otherwise large quantities of methane would be formed. The furnace 10 would ordinarily be constructed of steel to withstand the operating pressures, but is lined with any suitable inactive lining material 15 which prevents contact of the gases and the iron.

Methyl ether is soluble in water in large quantities at high pressure, but is only very slightly soluble at low pressure,

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Accordingly, we may separate the methyl ether from the resulting mixture as follows:

The mixture coming from the furnace at 16 is passed into the condenser 17 where it is cooled, the pressure being maintained at 25 atmospheres more or less. The water will condense and methyl ether will dissolve in it. If it should be found that at a particular operating pressure all of the methyl ether does not dissolve in the water formed as the result of the reaction, additional water may be added, for example, through an injector 18. The methyl ether may be separated from the resulting solution by passing the solution into a container 19 where the pressure is reduced, liberating the methyl ether as a gas. This gas can then be pumped off at 20 and used or stored in any suitable manner.

In practice, we find that the catalysts (A) and (B) need not be placed in the furnace as indicated above. Instead of being separated as two catalysts, the two substances may be intimately mixed so as to form, practically, a single substance, or they may be coarsely mixed, and the mixture distributed throughout the entire furnace. Even when so mixed, we prefer to heat the front part of the furnace to about 500° C. and the rear part to about 300° C.

We also find that, while a pressure of 125 atmospheres or more is preferable in the front part of the furnace, the pressure need not be maintained at this value throughout the furnace. It may, in fact, drop to 25 atmospheres at the rear end of the furnace and still give satisfactory results. If it is desired to operate with this pressure, the conformation of the furnace and/or the distribution of the catalyst may be such as to oppose considerable resistance to the passage of gas. This will then reduce the pressure in the back part of the furnace.

We may even dispense entirely with catalyst (A) and charge the furnace entirely with catalyst (B), in which case we use methyl alcohol as raw material instead of carbon monoxide and hydrogen. In this event the pressure throughout the entire furnace may be, for example, of the order of 25 atmospheres, but we prefer a higher operating pressure, such as 100 atmospheres because we find that the catalyst is more effective at higher pressure and hence the yield of the process is greater than at low pressures. The temperature in this case is preferably about 300° C.

Under some circumstances, as for example where alcohol is used as raw material as just described, we may mix some inert gas as a carrying agent with the material passed into the furnace. For instance, we may introduce carbon dioxide or any gas which does not affect the reaction and which is not acted upon by the catalyst. The inert gas is withdrawn from the apparatus after the methyl ether has become dissolved in the water. When such inert gas is used we employ an additional tank or container 21 through which the methyl ether solution and gas from the condenser are passed. The pressure is maintained at a sufficient value to retain the methyl ether in solution. The methyl ether solution may be drawn off into the tank 19 through the outlet 22 and the gas drawn off through the inlet 23 and returned to the furnace by the circulating pump 24.

The use of an inert carrying agent has various advantages. Its presence in the system allows the pressure in the furnace to be controlled more readily and thus facilitates the control of the speed of the process.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process of making methyl ether which comprises bringing carbon monoxide and hydrogen in contact with a hydrogenation catalyst and a dehydrating catalyst at high temperature and pressure.

2. A process of making methyl ether which comprises bringing methyl alcohol in contact with a dehydrating catalyst at high temperature and pressure.

3. A process according to claim 1 or 2 comprising dissolving the resulting methyl ether in water whilst under pressure.

4. A process according to claim 3 wherein the methyl ether which has been dissolved under pressure in water is subsequently separated from the solution by reducing the pressure of the solution to liberate the methyl ether.

5. A process according to claim 1 or 2 comprising cooling the resulting product at high pressure to dissolve the methyl ether and reducing the pressure to separate the methyl ether.

6. A process according to claim 1 wherein the temperature of the hydrogenation catalyst is maintained considerably above the temperature of the dehydrating catalyst.

7. A process according to claim 2 in which hydrous aluminium oxide is used as the dehydrating catalyst.

8. The improved process of making methyl ether substantially as hereinbefore described and illustrated.

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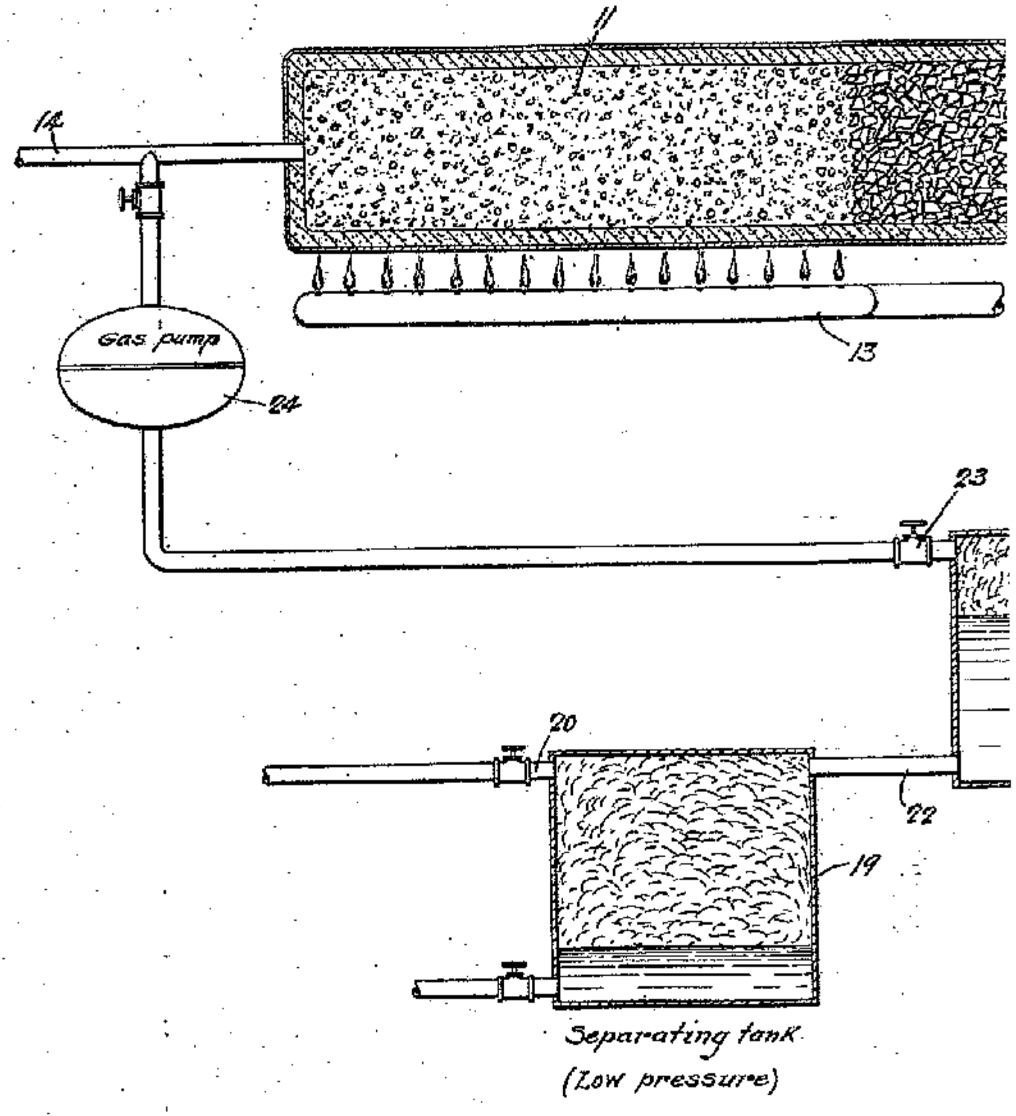
2nd Edition

[This Drawing is a full-size reproduction of the Original]



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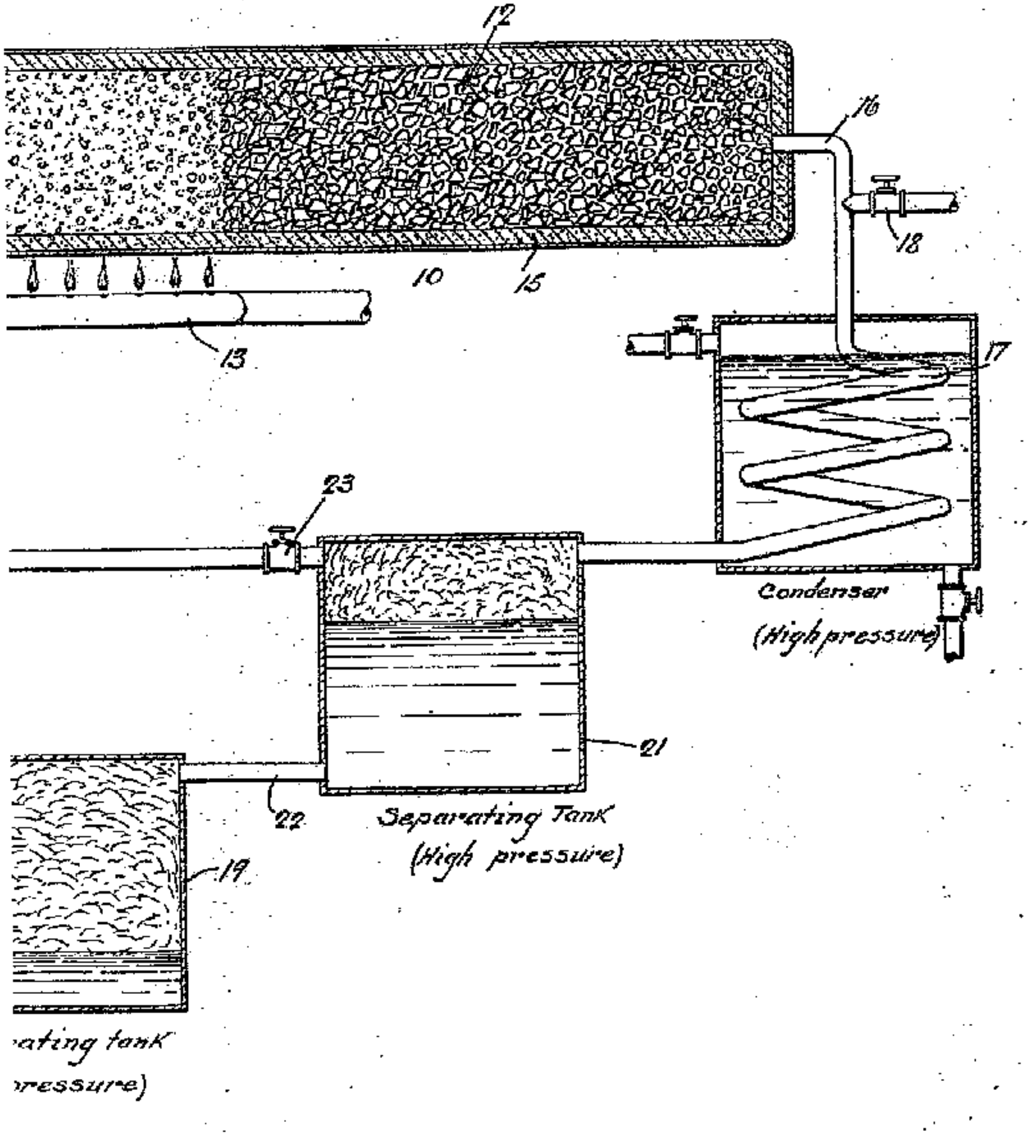

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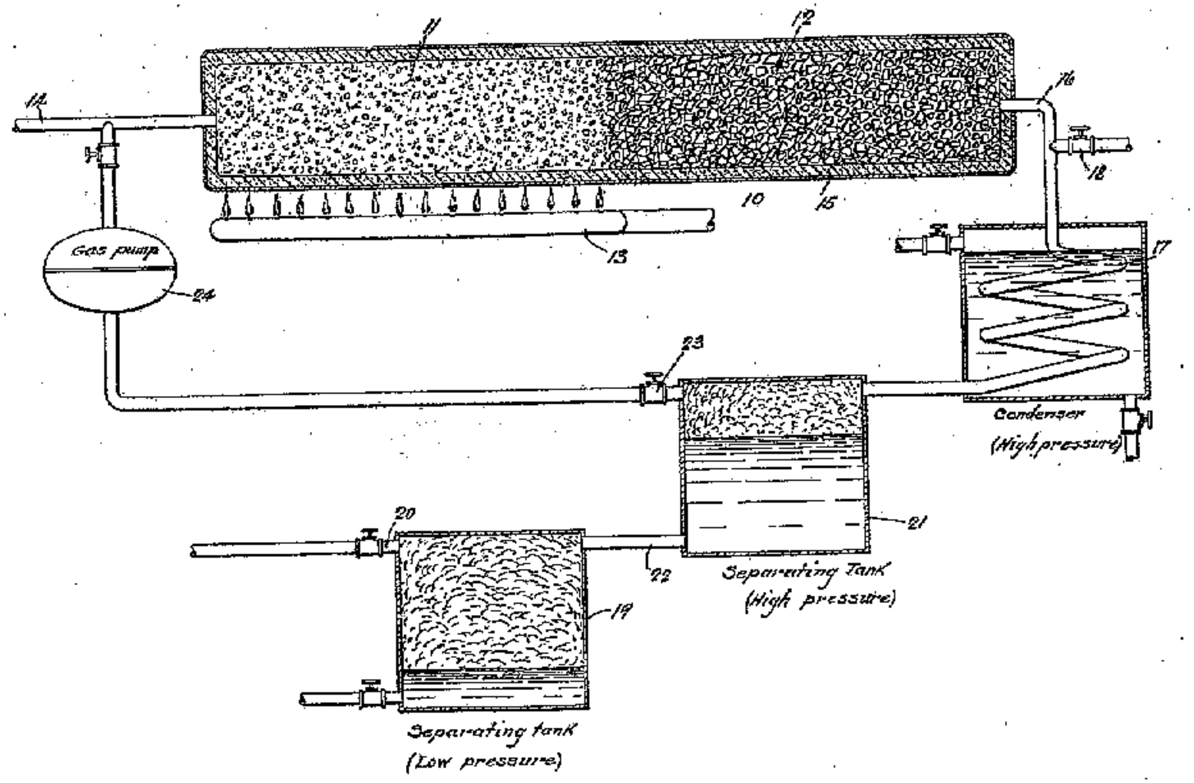

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