[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in or relating to the Manufacture of Methanol.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of Celanese House, 22 & 23, Hanover Square, London, W. 1, do hereby declare the nature of this invention to be as follows:—

This invention relates to the synthesis of methanol by the subjection of mixtures of carbon monoxide and hydrogen to the action of catalysts under elevated temperatures and pressure.

In practice it is usual to perform the synthesis of methanol by circulating the reaction gases repeatedly over the catalyst in a closed system, as a single passage over the catalyst results in very low conversion yields, usually too low to be economical. When, however, repeated circulation over the catalysts is performed, certain difficulties are liable to arise, it being usually found, for instance, that an equilibrium in the reaction is reached at a stage when a considerable quantity of the reaction gas is still unconverted. Moreover, undesirable side reactions are liable to occur through the repeated contacts of the conversion products with the catalyst. If steps are taken to remove the conversion products (e.g. by condensation) prior to the recirculation over the catalysts, these disadvantages are lessened to a certain degree, but it is found that the percentage conversion of the reaction gases is not increased to any large extent and that undesirable side reactions are still very liable to occur from repeated circulation of the small quantities of conversion products remaining in the reaction gases.

According to the invention, I have now found that these difficulties may be largely or entirely overcome by submitting the reaction gases to reaction by passing them successively through a number of reaction vessels arranged in series as an open system (i.e. not as a closed circuit). Further, by these means a substantially complete conversion of the reaction gases may be readily effected.

In performing the invention, I may employ any catalyst capable of promoting the synthesis of methanol. The reaction vessels may each be charged with a similar catalyst or catalysts or a different catalyst or catalysts may be employed in one or more of the reaction vessels. In certain cases it is advantageous to employ dissimilar catalysts in one or more of the reaction vessels, for instance in the production of methanol from reaction gases containing industrial gases containing CO or CO and hydrogen and where catalysts sensitive to poisoning by sulphur, (e.g. catalysts composed of or containing copper or copper compounds) are employed in one or more of the reaction vessels, it is advantageous to pass the reaction gases first through one or more reaction vessels charged with a less sensitive catalyst such for example as zinc oxide

The process of the invention may be performed under pressures and temperatures usually or hitherto employed for the synthesis of methanol with the particular catalyst or catalysts employed.

In its passage from one reaction vessel to the next, the reaction vapours may be treated to remove products of the conversion, as for instance by condensation such treatment may be effected between each pair of reaction vessels in the system.

The following example serves to illustrate one convenient method of preparing methanol in accordance with the invention:—

EXAMPLE.

A stream of water gas (or other industrial gas) containing between about 50 and 65% CO and 80 and 45% hydrogen is passed under a pressure of between 50 and 150 atmospheres through a chain of reaction vessels arranged in series. In the first reaction vessel or vessels of the series is placed a catalyst relatively insensitive to sulphur poisoning, e.g. pure zinc oxide. In the remaining reaction vessels of the series is placed a methanol catalyst containing copper or manganese, e.g. a mixture of copper oxide and zinc oxide. The temperature of the reaction in the reaction vessels is maintained at that commonly employed with the particular catalyst, usually such temperatures are between 200° and 540° C. and particularly between 300° and 450° C. between each pair of reaction vessels the reaction gases are treated to remove

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methanol as far as possible for instance by cooling and/or scrubbing with water, after which treatment the gases may, if necessary, be again raised to the reaction temperature by any suitable means before passing on to the next reaction vessel of the series. If desired, a sufficiently large number of reaction vessels may be employed in the series to ensure that substantially all the gas undergoes conversion; four or five reaction vessels are usually suitable for this purpose.

Dated this 4th day of June, 1929.
WHITEHEAD & STEPHENS,
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22 & 23, Hanover Square, London, W. 1.

COMPLETE SPECIFICATION.

Improvements in or relating to the Manufacture of Methanol.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of Celanese House, 22 & 23, Hanover Square, London, W. 1, 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 synthesis of methanol by the subjection of mixtures of carbon monoxide and hydrogen to the action of catalysts under elevated temperatures and pressure.

Numerous substances, particularly catalysts comprising copper, manganese or their compounds, are very active in promoting the synthesis of methanol, but their use on an industrial scale has been difficult or impossible owing to their sensitivity to sulphur poisoning. For this reason the industrial manufacture of methanol is usually performed in presence of zinc oxide or zinc oxide and chromium oxide.

The present invention provides a process whereby the catalysts sensitive to sulphur poisoning, and particularly catalysts comprising copper or manganese (or compounds of copper or manganese) can be successfully applied to the industrial manufacture of methanol.

According to the invention methanol is prepared by passing the reaction gases under the requisite conditions of temperature and pressure for the formation of methanol first over one or more catalyst masses composed of zinc oxide or zinc oxide and chromium oxide and thereafter over one or more methanol catalysts sensitive to sulphur poisoning and particularly catalysts comprising copper, manganese or compounds of copper or manganese.

In performing the reaction the reaction gases may be passed successively through a number of reaction vessels arranged in series as an open system (i.e. not as a closed circuit). By these means a substantially complete conversion of the reaction gases or vapours may be readily effected.

The process of the invention may be performed under pressures and temperatures usually or hitherto employed for the synthesis of methanol with the particular catalyst or catalysts employed.

In their passage from one reaction vessel to the next, the reaction vapours are treated to remove products of the conversion, as for instance by condensation.

The following example serves to illustrate one convenient method of preparing methanol in accordance with the invention:—

EXAMPLE.

A stream of water gas (or other industrial gas) containing between about 30 and 65% CO and 30 and 45% hydrogen is passed under a pressure of between 50 and 150 atmospheres through a chain of reaction vessels arranged in series. In the first reaction vessel or vessels of the series is placed a catalyst composed of pure zinc oxide. In the remaining reaction vessels of the series is placed a methanol catalyst containing copper or manganese, e.g. a mixture of copper oxide and zinc oxide. The temperature of the reaction in the reaction vessels is maintained at that commonly employed with the particular catalyst, usually such temperatures are between 200° and 540° C. and particularly between 300° and 450° C. Between each pair of reaction vessels the reaction gases are treated to remove methanol as far as possible for instance by cooling and/or scrubbing with water, after which treatment the gases may, if necessary, be again raised to the reaction temperature by any suitable means before passing on to the next reaction vessel of the series. If desired, a sufficiently large number of reaction vessels may be employed in the series to ensure that substantially all the gas undergoes conversion; four or five reaction vessels are usually suitable for this purpose.

Having now particularly described and

ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. Process for the manufacture of methanol from mixtures of hydrogen and carbon monoxide characterised in that the reaction gases are passed under the requisite conditions of temperature and pressure for the formation of methanol first over one or more catalyst masses composed of zinc oxide or zinc oxide and chromium oxide, and thereafter over one or more methanol catalysts sensitive to sulphur poisoning, particularly catalysts comprising copper, manganese, or compounds of copper or manganese.

2. Process according to claim 1 and wherein the reaction gases are passed successively through a number of reaction vessels arranged in series as an open chain (i.e. not as closed circuit).

3. Process according to claim 1 or 2 characterised in that the gases are caused to pass successively through a number of reaction vessels which number is sufficiently large to ensure that substantially all the gases undergo conversion.

4. Process for the manufacture of methanol substantially as described in the example.

5. Process for the synthesis of methanol substantially as hereinbefore described.

Dated this 25th day of February, 1930.

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