[Second Edition.]



# PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

## Improvements in the Synthetic Manufacture of Methanol and Higher Alcohols.

I, JAMES YATE JOHNSON, a British subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by the Badische Anilin & Soda Fabric, of Ludwigshafen-on-Rhine, Germany, a company incorporated according to German laws) to be as follows:—

Mixtures of carbon monoxide and hydrogen have repeatedly been exposed to the action of catalysts under conditions varying as to the nature of the catalysts and the temperature and pressure prevailing in the reaction with the result that methane, or liquid hydrocarbons have been obtained in so far as a reaction could be effected at all.

My foreign correspondents have now discovered that methanol can be obtained by the interaction of carbon monoxide and hydrogen at an elevated temperature and pressure and by the use of contact masses, provided the interior of the contact space be kept completely free from iron. In order to carry out this invention, the contact masses must be free from iron, the inner surface of the walls of the reaction chamber must not consist of iron and the gases must not carry any iron either in the form of fine particles or of volatile compounds of iron such as iron carbonyl. Provided the above conditions be observed, the other conditions may be varied within very wide limits. The nature of the contact masses may vary very considerably and the said masses may contain either metals or oxides or mixtures of more than one metal or more than one oxide or of metals or oxides and the proportion of carbon monoxide and hydrogen may be preferably so chosen that the volume of hydrogen prepondorates; other inert gases may be present, the pressure being preferably from 50 atmospheres upwards and the temperature between about 250 degrees and 600 degrees Centigrade, depending on the efficiency of the contact mass in each individual case.

The methanol produced in accordance with this invention is either pure or mixed with higher alcohols and other organic compounds containing oxygen, depending on the special conditions of working employed.

The following example will serve to further illustrate the nature of the invention but the invention is not limited thereto. The parts are by weight.

A tube capable of resisting high pressure is lined inside with copper and provided with a granular contact mass composed of equal molecular proportions of chromium oxide and manganese oxide and heated to 450 degrees Centigrade. A gas mixture containing about 80 *per cent.* by volume, of hydrogen and 20 *per cent.* by volume, of carbon monoxide, which has been carefully freed from any volatile iron compounds and suspended iron particles, is then passed through the said tube at a pressure of about 220 atmospheres while maintaining the temperature at 450 degrees Centigrade. The reaction gas is led through a cooler without releasing the pressure, when ample quantities of methanol will separate out. The residual gas may be led back into the tube after adding a fresh quantity of gas mixture.

With other contact masses, for example, such as are composed of copper and chromium oxide, or the oxides of zinc and chromium, the result is very similar. Under other conditions, for example with a contact mass containing besides oxides of heavy metals a small addition of potassium carbonate and preferably with a higher percentage of

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carbon monoxide and a reduced velocity of the gas current, higher alcohols such as propyl, butyl and amyl alcohols are formed besides methanol, the proportions varying according to the exact conditions, especially the temperature employed.

Contact masses containing oxides of vanadium, uranium, aluminium or other oxides non-reducible under the conditions of working may also be employed, or metals such as copper, silver, lead, zinc in conjunction with a metal oxide or a metal salt acting as a promoter or metal alloys for example, chromium and manganese, copper and zinc, and others.

Dated this 29th day of July, 1924.

JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London, W.C. 2,
Agents.

COMPLETE SPECIFICATION.

## Improvements in the Synthetic Manufacture of Methanol and Higher Alcohols.

I, JAMES YATE JOHNSON a British subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by the Badische Anilin & Soda Fabrik, of Ludwigshafen-on-Rhine Germany, a company incorporated according to German laws) and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

Mixtures of carbon monoxide and hydrogen have repeatedly been exposed to the action of catalysts under conditions varying as to the nature of the catalysts and the temperature and pressure prevailing in the reaction with the result that methane, or liquid hydrocarbons have been obtained (see Sabatier la catalyse en chimie organique 1913, pages 66 and 105, Lipinski who in the Specification of his Letters Patent No. 1325 A.D. 1913 used nickel and cobalt as a contact mass and the Specification of my prior Patent No. 20,488 A.D. 1913). According to the last named Specification No. 20,488 A.D. 1913 subordinate admixtures of organic compounds containing oxygen were also observed.

My foreign correspondents have now discovered that methanol either pure or mixed with other organic compounds containing oxygen, mainly higher alcohols, can be obtained with a highly satisfactory yield by the interaction of carbon monoxide and hydrogen at an elevated temperature and pressure and by the use of contact masses provided the interior of the contact space be kept free from iron. The process in accordance with this invention enables a continuous working to be effected with an easy control and for an extended period without undue deterioration of the contact mass.

In order to carry out this invention, the contact masses must be free from iron, the inner surface of the walls of the reaction chamber must not consist of iron and the gases entering the contact chamber must not carry any iron either in the form of fine particles or of volatile compounds of iron such as iron carbonyl thus avoiding any likelihood of contamination by iron in the contact chamber. Provided the above conditions be observed, the other conditions may be varied within very wide limits. The nature of the contact masses may vary very considerably and the said masses may contain either metals or oxides or mixtures of more than one metal or more than one oxide or of metals or oxides (of course excluding nickel and cobalt which as already stated lead to the production of methane). In addition to carbon monoxide and hydrogen, other gases may be present, the pressure being advantageously from about 50 atmospheres upwards and the temperature between about 250 degrees and 600 degrees Centigrade, depending on the efficiency of the contact mass in each individual case.

The following examples will serve further to illustrate the manner of carrying out the invention in practice, but the invention is not limited thereto. The parts are by weight.

EXAMPLE I.

A tube capable of resisting high pressure is lined inside with copper and provided with a granular contact mass composed of equal molecular proportions of chromium oxide and manganese oxide. A gas mixture containing about 80 *per cent.* by volume, of hydrogen and 20 *per cent.* by volume of carbon monoxide, which has been carefully freed from any volatile iron compounds and suspended iron particles, is then passed through the said tube at a pressure of about 220 atmospheres while maintaining the temperature at 450 degrees Centigrade. The

reaction gas is led through a cooler without releasing the pressure, when ample quantities of methanol will separate out. The residual gas may be led back into the tube after adding an appropriate amount of the desired fresh gases.

EXAMPLE 2.

A gas mixture composed of 70 *per cent.* of carbon monoxide, 25 *per cent.* of hydrogen and 5 *per cent.* of nitrogen, carefully freed from iron carbonyl, is passed at 400 degrees Centigrade and at a pressure of 200 atmospheres, over a contact mass consisting of an intimate mixture of chromium oxide and zinc oxide, placed in a tube-shaped reaction vessel, lined with aluminium and capable of resisting the pressure. On cooling the reaction gases while under pressure, ample quantities of nearly pure methanol are obtained. The operation can be carried on in a permanent way while circulating the gases under pressure as described in Example 1.

With other contact masses, for example, such as are composed of copper and chromium oxide, or the oxide of cadmium and vanadium, the result is very similar. Under other conditions, for example with a contact mass containing besides difficultly reducible metal oxides a small addition of potassium carbonate and preferably with a higher percentage of carbon monoxide and a reduced velocity of the gas current, higher alcohols such as propyl, butyl and amyl alcohols are formed besides methanol, the proportions varying according to the exact conditions, especially the temperature employed.

Contact masses containing oxides of uranium, aluminium or other oxides non-reducible under the conditions of working may also be employed, or metals such as copper, silver, lead, zinc in conjunction with a metal oxide or a metal salt acting as a promoter or metal alloys for example, chromium and manganese, copper and zinc, and others.

I am aware of my prior Patent Nos. 228,959, 229,714, 231,285, 227,147, 229,715, 238,319 and 237,030 and I lay claim to nothing claimed in the said specifications.

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. An improved process for the synthetic manufacture of methanol either pure or mixed with other organic compounds containing oxygen, mainly higher alcohols, or mixtures of the same, by catalytically hydrogenating carbon monoxide at an elevated temperature and pressure, the said process being characterised by the performance of the reaction in the absence of iron.

2. Methanol or other organic compounds containing oxygen, mainly higher alcohols or mixtures of the same, when produced in accordance with the foregoing claiming clause.

3. Methanol or other organic compounds containing oxygen, mainly higher alcohols or mixtures of the same when produced in accordance with the foregoing examples.

Dated this 26th day of February, 1925.

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