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[Second Edition.]

PATENT SPECIFICATION

Application Date: Sept. 19, 1927. No. 24,642/27.
Complete Left: June 18, 1928.
Complete Accepted: March 19, 1929.

308,181

1341)

PROVISIONAL SPECIFICATION.

CORRECTION OF CLERICAL ERROR.

SPECIFICATION No. 308,181.

The following correction is in accordance with the decision of the Assistant Comptroller, acting for the Comptroller-General, dated the eighth day of July, 1929:-

Page 3, line 100, *for* "265,503" *read* "263,503".

THE PATENT OFFICE,

23rd July, 1929.

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carbon oxides and hydrogen, even at ordinary or slightly elevated pressure, if particularly active copper catalysts be employed, preferably at temperatures of from 100 to 250 degrees Centigrade. If there be added to the copper, or to the copper compound such as cupric oxide, serving for the preparation of the catalyst, oxides or oxygen-containing substances of metals of groups 2—7 of the periodic system, catalysts of greatly increased activity are obtained. On the other hand, elements of group 8 must be excluded from the catalysts because, when these are present, the reduction proceeds beyond the production of methyl alcohol and leads to the formation of pure hydrocarbons. Copper catalysts with additions of (inter alia) oxides of beryllium, aluminium, zinc, yttrium, magnesium, lanthanum, cerium, thorium, lead, antimony, uranium, and manganese, have been found to be particularly effective. Generally speaking, it is advantageous to combine the copper or cupric oxide with two or more of the said oxides or oxygen-containing metallic compounds, especially when these latter belong to

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or in a larger or smaller proportion. Inert gases, such as nitrogen, methane and the like may also be present. In general, the gas is carefully freed beforehand from higher organic compounds, especially such as have a tendency to polymerisation and condensation, and also from contact poisons, as for example, metal carbonyls.

The resulting methyl alcohol is practically pure, and contains only very slight traces of compounds which react with bromine.

The following example will further illustrate the nature of the said invention which however is not limited thereto.

EXAMPLE.

A mixture of cupric oxide and magnesium oxide, in the proportion of 2 molecules of CuO to 1 molecule of MgO, is reduced with hydrogen for 30 hours at temperatures rising from 150° to 250° Centigrade. On passing a mixture of carbon monoxide and hydrogen, containing 33 per cent of CO over the resulting contact mass of 150° Centigrade, methyl alcohol is formed, and is separated by strongly cooling. It is clear and colour-

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PATENT SPECIFICATION

308,181

Application Date: Sept. 19, 1927. No. 24,642/27.

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PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Methanol.

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 I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany) to be as follows:—

It is already known that methyl alcohol can be prepared from mixtures of carbon oxides and hydrogen, by the application of high pressures and temperatures with the assistance of oxidic or metallic catalysts. Hitherto, the catalytic treatment of carbon oxides with hydrogen at ordinary pressure and with the employment of metals of group 8 of the periodic system, has only resulted in the production of hydrocarbons or of mixtures of hydrocarbons with various classes of organic compounds containing oxygen, the former substances predominating.

My foreign correspondents have now found that practically pure methyl alcohol may be prepared from mixtures of carbon oxides and hydrogen, even at ordinary or slightly elevated pressure, if particularly active copper catalysts be employed, preferably at temperatures of from 100 to 250 degrees Centigrade. If there be added to the copper, or to the copper compound such as cupric oxide, serving for the preparation of the catalyst, oxides or oxygen-containing substances of metals of groups 2—7 of the periodic system, catalysts of greatly increased activity are obtained. On the other hand, elements of group 8 must be excluded from the catalysts because, when these are present, the reduction proceeds beyond the production of methyl alcohol and leads to the formation of pure hydrocarbons. Copper catalysts with additions of (inter alia) oxides of beryllium, aluminium, zinc, yttrium, magnesium, lanthanum, cerium, thorium, lead, antimony, uranium, and manganese, have been found to be particularly effective. Generally speaking, it is advantageous to combine the copper or cupric oxide with two or more of the said oxides or oxygen-containing metallic compounds, especially when these latter belong to groups of the periodic system, the elements of which behave in as different a way as possible.

The catalysts are prepared by the joint precipitation of the copper compound and the additional substances from aqueous solution. Iron, or similar metals, or compounds of same, must be carefully excluded from the catalyst.

Prior to being used the catalysts are reduced with hydrogen or carbon monoxide, or mixtures of the two, in the presence of other gases, such as nitrogen, methane, carbon dioxide and the like, which do not hinder the reduction.

The working temperature may lie between 100 and 250 degrees Centigrade but it is advisable to keep it below 200 degrees Centigrade, since the output is generally lessened if higher temperatures be employed.

The proportion of carbon monoxide to hydrogen in the gases may be varied within wide limits. The hydrogen may be present either in the theoretical amount, or in a larger or smaller proportion. Inert gases, such as nitrogen, methane and the like may also be present. In general, the gas is carefully freed beforehand from higher organic compounds, especially such as have a tendency to polymerisation and condensation, and also from contact poisons, as for example, metal carbonyls.

The resulting methyl alcohol is practically pure, and contains only very slight traces of compounds which react with bromine.

The following example will further illustrate the nature of the said invention which however is not limited thereto.

EXAMPLE.

A mixture of cupric oxide and magnesium oxide, in the proportion of 2 molecules of CuO to 1 molecule of MgO, is reduced with hydrogen for 30 hours at temperatures rising from 150° to 250° Centigrade. On passing a mixture of carbon monoxide and hydrogen, containing 33 per cent of CO over the resulting contact mass of 150° Centigrade, methyl alcohol is formed, and is separated by strongly cooling. It is clear and colour-

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less, with a specific gravity of 0.792 at 15° Centigrade and a refraction index of 1.3308 at 17.5° Centigrade.

Dated this 19th day of September, 1927.
JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London,
W.C. 2,
Agents.

COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Methanol.

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 I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the laws of Germany) 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 production of methanol by hydrogenation of oxides of carbon.

It has already been suggested to produce methanol by the hydrogenation of oxides of carbon at an elevated pressure and at temperatures of 250° to 450° Centigrade with the aid of oxidic or metallic catalysts. The catalytic treatment of oxides of carbon with hydrogen at ordinary pressure and at temperatures of from 200° to 300° Centigrade with the employment of metals of the group 8 of the periodic system has hitherto only resulted in the production of hydrocarbons or of mixtures of hydrocarbons with various classes of organic compounds containing oxygen, the former substances predominating.

My foreign correspondents have now found that practically pure methanol may be prepared from mixtures of oxides of carbon and hydrogen even at ordinary or slightly elevated pressure, and preferably at temperatures of 100° to 250° Centigrade, when employing catalysts containing copper and one or more oxides of a metal from the groups 2 to 7 of the periodic system.

The said highly active catalysts required for carrying out the process according to the present invention are obtained by precipitating a solution of a mixture of a copper salt with one or more salts of the metals belonging to the groups 2 to 7 of the periodic system by means of aqueous solutions of alkalis at moderate temperatures for example below 30° Centigrade. The precipitates are freed from salts and alkali by thorough washing at about the same temperature and are then dried at temperatures of up to 250° to 350° Centigrade. Elements of the group 8 of the periodic system must be excluded from the catalysts since if the said elements are present, the hydrogenation proceeds beyond the formation of methanol and even pure hydrocarbons are formed. The hydroxides of beryllium, aluminium, zinc, yttrium, magnesium, lanthanum, cerium, thorium, lead, antimony, uranium and manganese have been found to be particularly suitable for the production of such catalysts when precipitated together with copper hydroxide from solutions of a mixture of a salt of the said metals with a salt of copper. Although during the drying process the copper hydroxide is converted into copper oxide, those catalysts in which as long as the precipitate is moist contain the copper entirely or for the greater part in the form of its blue hydroxide have been found to be considerably more active than those in which the copper is already contained during the precipitation or during the subsequent washing process completely or for the greater part as copper oxide. It is therefore necessary during the process of precipitating and washing out the precipitates to punctiliously avoid higher temperatures which would facilitate the dehydration of the copper hydroxide. The said catalysts are employed, either alone, or deposited on carriers.

The catalysts are reduced before being employed in the reaction proper. The heat which is thereby set free must be conducted away very carefully in order to obviate any spontaneous self-heating which would lead to sintering and which would reduce the activity of the catalysts. It has been found necessary to dilute the reducing agents, hydrogen or carbon monoxide or mixtures of both to a very considerable extent, say to about 90 to 98 per cent. with inert gases or vapours such as nitrogen, methane, water vapour or the like and further to carry out the reduction at the lowest workable temperatures. The reaction commences at between about 50° to 100° Centigrade at a workable rate. In order to attain the full activity of the catalysts, it is necessary after the greater part of the copper oxide has been reduced, to slowly increase the temperature up to 250° Centigrade, and to maintain this temperature for several hours.

The working temperature for the production of methanol may range between 100° and 250° Centigrade but the reaction is preferably carried out below 200° Centigrade since at higher temperatures the yield as a rule decreases.

The ratio of oxides of carbon to hydrogen in the gases varies within wide limits. The hydrogen may be present in the amount theoretically necessary, but it may also be employed in a greater or smaller amount; inert gases, such as nitrogen, methane and the like may also be present. The gas is as a rule previously carefully freed from catalyst poisons, viz. iron or other metals of the 8th group of the periodic system having an action similar to iron on mixtures of oxides of carbon and hydrogen, or compounds of such metals, for example, carbonyls, and from compounds of higher molecular weight having a tendency to condense or polymerise, and the catalysts are also kept free from these substances.

The mild conditions of the reaction for the greater part prevent undesired by-products being formed so that a methanol is produced of such purity that, in contradistinction to the methanol prepared at more elevated temperatures and pressures; it may be employed for many purposes without any purification by chemical treatment or by distillation. The process of the present invention therefore constitutes a very considerable advance in the state of the art.

The following Example will further illustrate how the said invention may be carried into practical effect, but the invention is not limited thereto.

EXAMPLE.

A mixture of copper oxide and magnesium oxide obtained by precipitating a solution containing 2 molecules of copper nitrate and 1 molecule of magnesium nitrate with dilute aqueous sodium hydroxide solution at 20° Centigrade, is reduced by means of a mixture of nitrogen and hydrogen containing 5 per cent. of the latter by heating for 30 hours beginning at a temperature of 100° Centigrade which is gradually raised to 250° Centigrade. If a mixture of carbon monoxide and hydrogen containing 33 per cent of the former be passed over the catalyst thus obtained at atmospheric pressure and at a temperature of 150° Centigrade, methanol is produced which is separated by cooling to low temperatures. It is limpid and colourless and has a specific weight of 0.792 at 15° Centigrade and a refraction index of 1.3308 at 17.5° Centigrade and contains only slight traces of compounds reacting with bromine.

It has already been proposed in Specification No. 2306 A.D. 1914 to employ in the hydrogenation or dehydrogenation of compounds containing carbon, including the oxides of carbon, as a catalytic agent an intimate mixture of copper with a promotor consisting of an oxide of oxygen salt of an earth metal including the rare earths or of beryllium, magnesium, manganese, uranium, vanadium, niobium, tantalum, chromium, boron or titanium. But the process of the present invention is based on the discovery that when employing the specific catalysts obtained in the manner herein described, according to which the catalysts are subjected to reduction by means of hydrogen or carbon monoxide or mixtures of both, which have been diluted with inert gases, substantially pure methanol is obtained, under very mild conditions, without the formation of substantial amounts of undesirable by-products since the catalysts thus obtained are particularly active.

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 I am aware of Specifications Nos. 265,503 and 108,855 and do not claim anything described or claimed therein but what I claim is:—

1. A process for the production of methanol by catalytic hydrogenation of oxides of carbon, which consists in operating at ordinary or only slightly elevated pressure, preferably at temperatures of between 100° and 250° Centigrade and employing catalysts containing copper and one or more oxides of a metal from the groups 2 to 7 of the periodic system either alone or deposited on carriers, the said catalyst being obtained by precipitating aqueous solutions of mixtures of the corresponding metal salts by means of alkalies at moderate temperatures, for example below 30° Centigrade, washing the precipitate thus obtained at about the same temperature and subjecting the said catalyst to a reduction treatment by means of hydrogen or carbon monoxide or mixtures thereof, which have been diluted with inert gases.

2. A specific method of carrying out the process claimed in claim 2, which consists in employing the said catalysts containing copper after subjection to a reduction treatment at temperatures commencing at 50° to 100° Centigrade and

gradually rising to 250° Centigrade.

3. A specific method of carrying out the process claimed in Claims 1 and 2 which consists in excluding iron or other metals of the group 8 of the periodic system having an action similar to iron on the mixtures of oxides of carbon and hydrogen, or compounds of such metals, from the catalysts and from the gases.

4. The process for the production of methanol substantially as described in the foregoing Example.

5. Methanol when obtained according to the preceding claiming clauses.

Dated this 18th day of June, 1928.
JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London,
W.C. 2,
Agents.

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[Wt. 51A.—125/6/1929.]