[Second Edition.]

# PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

## Improvements in the Catalytic Conversion of Mixtures of Carbon Monoxide and Hydrogen into Valuable Organic Compounds Containing more than one Carbon Atom in the Molecule.

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) to be as follows:—

The present invention is an improvement in or modification of the process for the manufacture and production of methanol or other organic compounds containing oxygen by catalytic hydrogenation of carbon oxides under pressure and at an elevated temperature and in the presence of a catalyst capable of causing the formation of methanol or other organic compounds by employing gas mixtures which contain a high percentage of gases not required for the reaction and working in a circulatory system with a continuous removal of part of the circulating gases enriched in inert gases and its replacement by fresh gas mixture in such proportion as to maintain a substantially constant composition of the circulating gas mixture as described and claimed in the Specification No. 266,405.

My foreign correspondents have now found that when catalytically producing oxygen-containing organic compounds, or hydrocarbon containing more than one carbon atom from such gas mixtures of carbon monoxide and hydrogen as are free or low in gases not taking part in the reaction, the injurious action of the heat of the exothermic reaction, or the deposition of carbon or extensive formation of methane is prevented by carrying out the operation in a circulatory system and adding extraneous gases so that the circulating gases always contain a certain proportion of the said gases, such as nitrogen, methane, ethane, rare gases and the like, to the extent of 40 per cent. or more.

The extraneous gases may be introduced into the mixture of carbon monoxide and hydrogen either previously to, or at the commencement of, or during, the reaction.

The excessive heat of the reaction may also be partially eliminated by the employment of heat absorbing media, as for example by disposing the catalyst in tubes which are bathed by the colder gases which have not entered into the reaction.

The lowering of the partial pressure of carbon monoxide and hydrogen by the admixture of extraneous gases may be counteracted by raising the total pressure. The operation may be carried out under elevated pressure, such for example as 20, 50, 200, 1000 or more atmospheres.

The process according to the present invention offers great advantages, especially in the production of liquid hydrocarbons with the aid of catalysts containing iron and cobalt, but it may also be carried out with advantage in other cases as for example in the production of organic oxygen compounds containing more than one carbon atom, such as acids, esters, alcohols, ketones, and the like, with the assistance of catalysts containing, for example, iron, cadmium and copper, or potassium, zinc and chromium or zinc, chromium and manganese and the like.

If an initial gas rich in methane, as for example coal gas, be available, the amount of extraneous gas is considerably lessened at the commencement by the catalytic conversion of the methane, with water, or oxygen, into carbon monoxide and hydrogen, so that the amount of fresh extraneous gas introduced into the circulation, in which a certain proportion of extraneous gas already exists, will be minimised.

It is advisable to free the fresh gas more or less completely from carbon dioxide, sulphur compounds and iron carbonyl.

The following Examples will further

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illustrate the nature of the said invention which however, is not limited thereto. The parts are by weight.

EXAMPLE 1.

A gaseous mixture consisting of 65 per cent. of methane, 10 per cent. of nitrogen, 10 per cent. of carbon monoxide and 15 per cent. of hydrogen is circulated, at 290° Centigrade and 50 atmospheres pressure, over a catalyst containing 100 parts of copper and 0.5 part of potassium in the form of potassium carbonate per 100 parts of iron. The portions of carbon monoxide and hydrogen consumed during the reaction are replaced, in the circulation, by continuously pumping in water gas, of approximately 39 per cent. of carbon monoxide, 58 per cent. of hydrogen and 3 per cent. of nitrogen and methane, purified in the usual manner. The operation proceeds smoothly and furnishes a good yield of partly liquid and partly gaseous higher hydrocarbons, which may be recovered, in any known and suitable manner, by cooling under pressure, or also by the use of absorbents. Undesirable secondary reactions, decomposition of carbon monoxide with deposition of carbon and formation of methane, do not occur.

On the other hand, when working, under otherwise identical conditions, with a gaseous mixture consisting of 40 per cent. of carbon monoxide and 60 per cent. of hydrogen, at 12.5 atmospheres, the catalyst, after at first effecting the formation of hydrocarbons, very soon becomes quite useless as the result of local superheating and the deposition of carbon.

EXAMPLE 2.

A solution containing 100 parts of iron 40 parts of copper and 15 parts of cadmium, in the form of nitrates, is precipitated with potassium carbonate, the resulting precipitate being washed until the content of potassium is reduced to 0.5 part per 100 parts of iron, whereupon it is dried and granulated.

About 3 litres of the resulting catalyst are charged into a pressure tube lined with manganese copper and mounted in a metal bath which can be heated or cooled as required. The arrangement of the pipes is such that an exchange of heat can be effected between the gases flowing respectively into and out of the catalyst chamber. The prewarmed gas to be subjected to the reaction is passed through a tube disposed in the longitudinal axis of the catalyst tube, and thereby serves as a medium for cooling the catalyst, whilst at the same time it becomes heated to the temperature necessary for the reaction. If a mixture consisting of 20 per cent. of carbon monoxide, 20 per cent. of hydrogen, 55 per cent. of methane and 5 per cent. of nitrogen, be circulated through this catalyst tube, under a pressure of 350 atmospheres, the temperature being maintained at about 320° Centigrade, a continuous production of abundant quantities of liquid hydrocarbons will be obtained, together with oxygen products such as ethyl alcohol, higher alcohols, and esters, provided amounts of fresh gas, about 50 per cent. of carbon monoxide and 50 per cent. of hydrogen, corresponding to the gas consumption be introduced into the circulation.

EXAMPLE 3.

A gaseous mixture consisting of 20 per cent. of carbon monoxide, 30 per cent. of hydrogen, 40 per cent. of methane and 10 per cent. of nitrogen, is circulated at 450° Centigrade and 350 atmospheres over a catalyst prepared by fusing 3 parts of potassium bichromate with 1 part of manganese oxide and 1 part of zinc oxide. Water gas, freed from carbon dioxide and sulphur compounds, and containing only inconsiderable amounts of extraneous gases is used as the replenishing gas. The operation proceeds smoothly and continuously and furnishes a good yield of a product consisting of methyl alcohol, isobutyl alcohol, higher alcohols and cyclic ketones. In order to maintain the amount of extraneous gas always at say 50 per cent. or thereabouts during the circulation, only small amounts of the circulating gases need be continuously withdrawn from the system, since only small amounts of extraneous gas are introduced with the replenishing gas.

Dated this 9th day of February, 1928.

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

COMPLETE SPECIFICATION.

## Improvements in the Catalytic Conversion of Mixtures of Carbon Monoxide and Hydrogen into Valuable Organic Compounds Containing more than one Carbon Atom in the Molecule.

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 inven-

tion (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:—

The present invention is an improvement on or modification of the process for the manufacture and production of methanol or other organic compounds containing oxygen by catalytic hydrogenation of carbon oxides under pressure and at an elevated temperature and in the presence of a catalyst capable of causing the formation of methanol or other organic compounds by employing gas mixtures which contain a high percentage of gases not required for the reaction and working in a circulatory system with a continuous removal of part of the circulating gases enriched in inert gases and its replacement by fresh gas mixture in such proportion as to maintain a substantially constant composition of the circulating gas mixture as described and claimed in Specification No. 266,405.

It has already been proposed to produce a liquid condensate containing methanol, ethyl and higher alcohols, saturated and unsaturated ketones and other organic compounds by passing a gas having the approximate composition:—50 per cent. of hydrogen, 30 per cent. of methane, 12 per cent. of carbon monoxide, 4 per cent. of ethylene and 4 per cent. of nitrogen at a temperature of 400° Centigrade and under a pressure of 800 atmospheres over a catalyst prepared by kneading 3 parts of cobalt hydroxide with 1 part of uranium oxide and 1 part of manganese oxide and then drying the mass thus obtained and reducing it to grains, thereupon soaking it with concentrated potash solution. A process has further been suggested for the simultaneous production of methanol and liquid hydrocarbons according to which a gas mixture containing ethylene or its homologues in a proportion of about 10 to 40 per cent. of the total volume of the gas mixture in addition to carbon monoxide and hydrogen is passed over a methanol forming catalyst and the mixture of water gas with a gas from the distillation of coal has been proposed as suitable for the said purpose.

My foreign correspondents have now found that when catalytically producing oxygen-containing organic compounds or hydrocarbons containing more than one carbon atom from such gas mixtures of carbon monoxide and hydrogen as are free from or low in extraneous gases not taking part in the reaction and which contain the carbon monoxide and hydrogen in the requisite proportions for the synthesis, the injurious action of the heat of the exothermic reaction, or the deposition of carbon, or extensive formation of methane is prevented, by carrying out the operation in a circulatory system and mixing such extraneous gases with the gases partaking in the reaction, so that the circulating gases always contain at least 40 per cent. of the said gases, such as nitrogen, methane, ethane, rare gases and the like, while the fresh gases admitted into the cycle consist of a mixture of carbon monoxide and hydrogen substantially free from extraneous gases not taking part in the reaction. Whenever percentages of gas are referred to in the present specification these are always by volume.

The extraneous gases are introduced into the mixture of carbon monoxide and hydrogen either previously to, or at the commencement of, and if desired also during the reaction.

The excessive heat of the reaction may also be partially eliminated by the employment of heat absorbing media, as for example by disposing the catalyst in tubes which are bathed by the colder gases which have not yet entered into the reaction.

The lowering of the partial pressure of carbon monoxide and hydrogen by the admixture of extraneous gases may be counteracted by raising the total pressure. The operation may be carried out under elevated pressure, such for example as 20, 50, 200, 1000 or more atmospheres, and as a rule, the higher the pressure, the higher will be the molecular weight of the products obtained.

The process according to the present invention offers great advantages, especially in the production of liquid hydrocarbons with the aid of catalysts containing iron and cobalt, but it may also be carried out with advantage in other cases as for example in the production of organic oxygen compounds containing more than one carbon atom, such as acids, esters, alcohols, ketones and the like, with the assistance of catalysts containing, for example, iron, cadmium, and copper, or potassium, zinc and chromium or zinc, chromium and manganese and the like.

If an initial gas rich in methane, as for example coal gas, be available, the amount of extraneous gas is considerably lessened at the commencement by the catalytic conversion of the methane, with water, or oxygen, into carbon monoxide and hydrogen, so that the amount of fresh extraneous gas introduced into the circu-

lation, in which a certain proportion of extraneous gas already exists, will be minimised and further extraneous gases must therefore be added. Thereafter to replenish the gases consumed, fresh gases are admitted into the cycle consisting of a mixture of carbon monoxide and hydrogen substantially free from extraneous gases not taking part in the reaction.

It is advisable to free the fresh gas more or less completely from carbon dioxide, sulphur compounds and iron carbonyl.

The following Examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these examples. The parts are by weight.

EXAMPLE 1.

A gaseous mixture consisting of 65 per cent. of methane, 10 per cent. of nitrogen, 10 per cent. of carbon monoxide and 15 per cent. of hydrogen is circulated, at 290° Centigrade and 50 atmospheres pressure over a catalyst containing 100 parts of iron, 100 parts of copper and 0.5 part of potassium in the form of potassium carbonate. The portions of carbon monoxide and hydrogen consumed during the reaction are replaced, in the circulation, by continuously pumping in water gas, of approximately 39 per cent. of carbon monoxide 58, per cent. of hydrogen and 3 per cent. of nitrogen and methane, purified in the usual manner. The operation proceeds smoothly and furnishes a good yield of partly liquid and partly gaseous higher hydrocarbons, which may be recovered, in any known and suitable manner, by cooling under pressure, or also by the use of absorbents. Undesirable secondary reactions, decomposition of carbon monoxide with deposition of carbon and formation of methane, do not occur.

On the other hand, when working, under otherwise identical conditions, with a gaseous mixture consisting of 40 per cent. of carbon monoxide and 60 per cent. of hydrogen, at 12.5 atmospheres, the catalyst, after at first effecting the formation of hydrocarbons, very soon becomes quite useless as the result of local superheating and the deposition of carbon.

EXAMPLE 2.

A solution containing 100 parts of iron, 40 parts of copper and 15 parts of cadmium, in the form of nitrates, is precipitated with potassium carbonate, the resulting precipitate being washed until the content of potassium is reduced to 0.5 part per 100 parts of iron, whereupon it is dried and granulated.

About 3 litres of the resulting catalyst are charged into a pressure tube lined with manganese copper and mounted in a metal bath which can be heated or cooled as required. The arrangement of the pipes is such that an exchange of heat can be effected between the gases flowing respectively into and out of the catalyst chamber. The prewarmed gas to be subjected to the reaction is passed through a tube disposed in the longitudinal axis of the catalyst tube, and thereby serves as a medium for cooling the catalyst, whilst at the same time it becomes heated to the temperature necessary for the reaction. If a mixture consisting of 20 per cent. of carbon monoxide, 20 per cent. or hydrogen, 55 per cent. of methane and 5 per cent. of nitrogen, be circulated through this catalyst tube, under a pressure of 350 atmospheres, the temperature being maintained at about 320° Centigrade, a continuous production of abundant quantities of liquid hydrocarbons will be obtained, together with oxygen products such as ethyl alcohol, higher alcohols, and esters, provided amounts of fresh gas, about 50 per cent. of carbon monoxide and 50 per cent. of hydrogen, corresponding to the gas consumption be introduced into the circulation.

EXAMPLE 3.

A gaseous mixture consisting of 20 per cent. of carbon monoxide, 30 per cent. of hydrogen, 40 per cent. methane and 10 per cent. of nitrogen, is circulated at 450° Centigrade and 350 atmospheres over a catalyst prepared by fusing 3 parts of potassium bichromate with 1 part of manganese oxide and 1 part of zinc oxide. Water gas containing about 40 per cent. of carbon monoxide and 55 to 60 per cent. of hydrogen, freed from carbon dioxide and sulphur compounds, and containing only inconsiderable amounts of extraneous gases is used as the replenishing gas. The operation proceeds smoothly and continuously and furnishes a good yield of a product consisting of methyl alcohol, isobutyl alcohol, higher alcohols and cyclic ketones. In order to maintain the amount of extraneous gas always at say 50 per cent. or thereabouts during the circulation, only small amounts of the circulating gases need be continuously withdrawn from the system, since only small amounts of extraneous gas are introduced with the replenishing gas.

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 improvement in or modification of the invention described and claimed in the Specification No. 266,405, for catalytically producing oxygen-containing organic compounds or hydrocarbons con-

taining more than one carbon atom in the molecule from such gas mixtures of carbon monoxide and hydrogen as are free from or low in extraneous gases not taking part in the reaction and which contain the carbon monoxide and hydrogen in the requisite proportions for the synthesis, which consists in carrying out the operation in a circulatory system and mixing such extraneous gases with the gases partaking in the reaction so that the circulating gases always contain at least 40 per cent. by volume of such extraneous gases whilst the fresh gases admitted into the cycle consist of a mixture of carbon monoxide and hydrogen substantially free from extraneous gases not taking part in the reaction.

2. The process for catalytically producing oxygen-containing organic compounds or hydrocarbons containing more than one carbon atom in the molecule substantially as described in each of the foregoing Examples.

3. Oxygen-containing organic compounds or hydrocarbons containing more than one carbon atom in the molecule when obtained according to the preceding claiming clauses.

Dated this 5th day of November, 1928.

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

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