[Second Edition.]

PATENT SPECIFICATION

Application Date : June 3, 1937. *No. 15439/37.* **496,880**

Complete Specification Left : May 27, 1938.

Complete Specification Accepted : Dec. 5, 1938.

PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Valuable Hydrocarbons and their Derivatives containing Oxygen from Carbon Monoxide and Hydrogen.

I, GEORGE WILLIAM 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 organised under the Laws of Germany) to be as follows:—

In the specification No. 473,932 there is described and claimed a process for the conversion of carbon-monoxide and hydrogen into liquid, solid and gaseous hydrocarbons or their derivatives containing oxygen according to which catalysts are used which have been prepared before the said conversion by thermal treatment of iron compounds or substances containing the same, at temperatures above 600° Centigrade but below the melting or sublimation point of the iron compound or of the iron resulting from this treatment and by a treatment with reducing gases. Advantageously the thermal treatment is performed in the presence of reducing gases.

In the said specification it is also stated that the thermal treatment may also be carried out in two or more stages, the iron compounds first being heated to above 600° Centigrade in the presence of non-reducing gases, as for example nitrogen or air, and then treated with reducing gases. The treatment with reducing gases in this case may take place at lower temperatures, as for example 300°, 400°, 450° or 500° Centigrade.

In the specification No. 474,448 there is described a special method of preparing catalysts for the conversion of carbon monoxide with hydrogen according to which a metal of the iron group is precipitated in the form of a compound easily reducible to metal by heating with hydrogen, there is added a compound of another metal which is converted by heating into an oxide which cannot be reduced to metal with hydrogen below 900° Centigrade, and finally the mixture is heated in the presence of a gas having a reducing action at such a high temperature above 500° Centigrade and for such a long time that a partial sintering takes place.

My foreign correspondents have now found that catalysts of high activity and good stability are obtained by first reducing the said metal compounds in the presence of reducing gases at an elevated temperature below 500° Centigrade, no sintering thus taking place, and then treating them in the presence of non-oxidising (inert or even reducing) gases or *in vacuo* at a temperature above 500° Centigrade, advantageously above 600° Centigrade, in such manner that at least a partial sintering of the reduced catalyst takes place. At the moderately elevated temperature below 500° Centigrade, a reduction of the metal compound to metal takes place, while at the higher temperature then employed a sintering of the reduced substance takes place. Both the treatment with reducing gases and the subsequent treatment in the presence of non-oxidising gases or *in vacuo* may be effected in one or more stages.

The reduction of the metal compounds is advantageously carried out between about 300° and 450° Centigrade or higher, while for the subsequent thermal treatment of the reduced substances in the presence of non-oxidising gases or *in vacuo* temperatures of for example 600°, 700°, 800°, 1000° Centigrade or higher may be used with advantage.

As reducing gases there may be mentioned in particular hydrogen or gases containing hydrogen, as for example hydrogen in admixture with methane, or gases yielding hydrogen; carbon monoxide or hydrocarbons, such as methane and ethane, may, however, also be used.

As non-oxidising gases for the thermal treatment above 500° Centigrade there may be mentioned nitrogen, argon, hydrogen and the like or mixtures of the same.

The gases used in the thermal treatment above 500° Centigrade should not effect any oxidation of the reduced substances.

[*Price* 1/-]

If small amounts of oxidising constituents are present therein, they may be rendered non-injurious by the addition of small amounts of reducing gases.

The said reduction of the catalysts, and also the thermal treatment at above 500° Centigrade, may be carried out at atmospheric, reduced or increased pressure, as for example at 2, 5, 20, 100 atmospheres or more, and the pressure may be identical or different in the two stages.

The following Example will further illustrate the nature of this invention but the invention is not restricted to this Example.

EXAMPLE.

Precipitated iron hydroxide is stirred with 3 per cent of aluminium hydroxide (calculated on metallic iron), dried and reduced at 450° Centigrade with hydrogen until there is no further formation of water. The reduced mass is heated for about 3 hours at 850° Centigrade with nitrogen free from oxygen, cooled in a stream of nitrogen and then charged in the form of pieces into a reaction vessel through which a mixture of carbon monoxide and hydrogen in the ratio of 1:2 is led at about 320° Centigrade under a pressure of 15 atmospheres. In addition to gaseous hydrocarbons, there are thus formed abundant amounts of liquid hydrocarbons and smaller amounts of solid hydrocarbons. The liquid hydrocarbons contain a few per cent. of compounds containing oxygen.

Dated this 3rd day of June, 1937.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Valuable Hydrocarbons and their Derivatives containing Oxygen from Carbon Monoxide and Hydrogen.

I, GEORGE WILLIAM 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 organised 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:—

In the specification No. 473,932 there is described and claimed a process for the conversion of carbon monoxide and hydrogen into liquid, solid and gaseous hydrocarbons or their derivatives containing oxygen according to which catalysts are used which have been prepared before the said conversion by thermal treatment of iron compounds or substances containing the same, at temperatures above 600° Centigrade but below the melting or sublimation point of the iron compound or of the iron resulting from this treatment and by treatment with reducing gases. The treatment with reducing gases may be effected simultaneously or subsequently to the thermal treatment.

In the said specification as open to public inspection under Section 91 it is stated that the thermal treatment is effected at such a high temperature ranging above 500° Centigrade and for such a long duration that a sintering of the catalyst takes place.

In the specification No. 474,448 there is described a special method of preparing catalysts for the conversion of carbon monoxide with hydrogen according to which a metal of the iron group is precipitated in the form of a compound easily reducible to metal by heating with hydrogen, there is added a compound of another metal which is converted by heating into an oxide which cannot be reduced to metal with hydrogen below 900° Centigrade, and finally the mixture is heated in the presence of a gas having a reducing action at such a high temperature above 500° Centigrade and for such a long time that a partial sintering takes place.

My foreign correspondents have now found that catalysts of high activity and good stability are obtained by first reducing compounds of metals of the iron group reducible to the metal at a temperature below 500° Centigrade, in the presence of reducing gases at an elevated temperature below 500° Centigrade, no sintering thus taking place, and then treating them in the presence of non-oxidising (inert or even reducing) gases or *in vacuo* at such a temperature above 500° Centigrade but below the melting point of the reduced substance, advantageously above 600° Centigrade, in such a manner, i.e., for such a long time, that at the particular temperature employed at least a partial sintering of the reduced substance takes place. At the moderately elevated temperature below 500° Centigrade, a reduction of the metal compound to metal takes

place, while at the higher temperature then employed a sintering of the reduced substance takes place. Both the treatment with reducing gases and the subsequent treatment in the presence of non-oxidising gases or *in vacuo* may be effected in one or more stages.

By the term "partial sintering" is meant the agglomeration of the originally separated particles of a solid substance by the action of heat to form coherent masses having a substantial porosity.

The reduction of the metal compounds is advantageously carried out between about 300° and 450° Centigrade or higher while for the subsequent thermal treatment of the reduced substances in the presence of non-oxidising gases or *in vacuo* temperatures of for example 600°, 700°, 800°, 1000° Centigrade or higher may be used with advantage.

As reducing gases there may be mentioned in particular hydrogen or gases containing hydrogen, as for example hydrogen in admixture with methane, or gases yielding hydrogen; carbon monoxide or hydrocarbons, such as methane and ethane, may, however, also be used.

As non-oxidising gases for the thermal treatment above 500° Centigrade there may be mentioned nitrogen, argon, hydrogen and the like or mixtures of the same.

The gases used in the thermal treatment above 500° Centigrade should not effect an appreciable oxidation of the reduced substances. If small amounts of oxidising constituents are present therein, they may be rendered non-injurious by the addition of small amounts of reducing gases.

The said reduction of the catalysts, and also the thermal treatment at above 500° Centigrade, may be carried out at atmospheric, reduced or increased pressure, as for example at 2, 5, 20, 100 atmospheres or more, and the pressure may be identical or different in the two stages.

The conversion of the carbon monoxide with the hydrogen in the presence of the catalyst thus obtained is effected at temperatures above 150° preferably between 200° and 450° Centigrade. Atmospheric pressure or subatmospheric pressure may be employed, but it is preferable to employ increased pressures such as 5, 10, 20, 50, 100 atmospheres or more.

The products obtained by the said conversion are hydrocarbons containing more than one carbon atom in the molecule. in particular liquid and solid, but also gaseous hydrocarbons and/or non-gaseous, i.e. liquid or solid oxygen-containing derivatives of hydrocarbons, such as alcohols, ketones, esters. acids, aldehydes and the like.

The following Example will further illustrate how the said invention may be carried out in practice but the invention is not restricted to this Example.

EXAMPLE.

Precipitated iron hydroxide is stirred with 3 per cent. of aluminium hydroxide (calculated on metallic iron), dried and reduced at 450° Centigrade with hydrogen until there is no further formation of water. The reduced mass is heated for about 3 hours at 850° Centigrade with nitrogen substantially free from oxygen, cooled in a stream of nitrogen and then charged in the form of pieces into a reaction vessel through which a mixture of carbon monoxide and hydrogen in the ratio 1:2 by volume is led at about 320° Centigrade under pressure of 15 atmospheres. In addition to gaseous hydrocarbons, there are thus formed abundant amounts of liquid hydrocarbons and smaller amounts of solid hydrocarbons. The liquid hydrocarbons contain a few per cent. of non-gaseous oxygen-containing derivatives of hydrocarbons.

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. A process for the conversion of carbon monoxide and hydrogen into hydrocarbons containing more than one carbon atom in the molecule and/or non-gaseous oxygen-containing derivatives of hydrocarbons which comprises contacting the said carbon monoxide and hydrogen at a reacting temperature with a catalyst prepared prior to the conversion by reducing a compound of a metal of the iron group, reducible to the metal at a temperature below 500° Centigrade, by treatment at an elevated temperature below 500° Centigrade with a reducing gas and then treating the reduced substance in the absence of an oxidising gas at such a high temperature above 500° Centigrade but below the melting point of the reduced substance and for such a long time that at least partial sintering of the reduced substance takes place.

2. In the process as claimed in claim 1, contacting the carbon monoxide and hydrogen with a catalyst prepared by reducing a reducible compound of an iron group metal at a temperature below 500° Centigrade and then heating the reduced substance to a temperature above 600° Centigrade.

3. In the process as claimed in claim 2, employing as reducible compound of an iron group metal a reducible iron compound.

4. The process for the conversion of carbon monoxide and hydrogen into hydrocarbons containing more than one carbon atom and non-gaseous oxygen-containing derivatives of hydrocarbons substantially as described in the foregoing Example.

5. Hydrocarbons containing more than one carbon atom in the molecule and non-gaseous oxygen-containing derivatives of hydrocarbons when obtained by the process particularly described and ascertained.

Dated this 27th day of May, 1938.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2.
Agents.

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