[Second Edition.]

PATENT SPECIFICATION

Application Date: Sept. 21, 1937. *No. 25589/37.* **506,064**

Complete Specification Left: Aug. 22, 1938.

Complete Specification Accepted: May 22, 1939.

PROVISIONAL SPECIFICATION.

Improvements in Reacting Carbon Monoxide with 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:—

My foreign correspondents have found that by the reaction of carbon monoxide and hydrogen at elevated temperature, valuable products, in particular low-boiling hydrocarbons of the boiling range of benzines and heavy benzines are obtained by using as catalysts sintered metals of the iron group to which there are added alkali compounds which in aqueous solution have a neutral or acid reaction and which are practically undecomposed at temperatures up to 1000° Centigrade.

The sintered metals of the iron group, of which iron is preferably employed, may be prepared in particular from metal powders or porous metals.

The metal powders may be prepared in any suitable way, as for example by decomposition of organo-metallic compounds, such as iron carbonyl, or by reduction of pulverulent metal oxides or hydroxides or by the decomposition and reduction of suitable other metal compounds, such as carbonates, nitrates or oxalates.

Porous metals suitable for sintering can be prepared by reduction of pieces of metal oxides or hydroxides or by pressing metal powders, as for example pulverulent carbonyl iron.

The sintering of the metals is effected by heating to temperatures above 500° Centigrade, advantageously above 600°, as for example at 700°, 800°, 900° or 1000° Centigrade, in such a manner, i.e. for so long a time, that a visible decrease in volume (preferably more than 10 per cent. takes place); in the case of metal powders the powder particles agglomerate and in the case of porous metals there is a decrease in porosity. Non-oxidising gases, such as nitrogen, may be present during the sintering. In many cases it is advantageous to work in the presence of reducing gases, such as hydrogen or gases containing hydrogen. The sintering may also be carried out *in vacuo*. When starting from reducible metal compounds, these may first be converted into the metals by treatment at relatively low temperatures, as for example, at from 400° to 500° Centigrade, with reducing gases, whereby no sintering takes place, and then sintered at above 500°, advantageously above 600° Centigrade in the presence of non-oxidising gases or *in vacuo*. The reduction and sintering may, however, also be effected in one single operation, for example by treating an oxide at temperatures above 500° (as for example 850°) Centigrade with reducing gases for such a length of time that not only a reduction but also a sintering of the metal formed by the reduction takes place. The speed of flow and the partial pressure of the hydrogen should be adapted to the speed of reduction of the metal compound treated.

The sintering may also be effected in different stages of pressure, for example by first working at atmospheric pressure and then, at the same or a different temperature, under increased pressure, as for example, at 2, 5, 10, 50, 100 atmospheres or more. The sintering in one stage may also be effected under increased pressure.

As alkali compounds to be added there may be mentioned in particular alkali halides, as for example potassium chloride, potassium bromide, sodium chloride, or sodium fluoride. Other alkali compounds which are practically undecomposed at temperatures up to 1000° Centigrade may also be added, as for example the non-alkaline reacting phosphates of sodium and potassium, such as monosodium phosphate and monopotassium phosphate. Generally speaking the said alkali compounds are added in an amount of 0.5, 2, 5, 10, 15 per cent. by weight or more (with reference to the metal used). In many cases, additions of 0.1 per cent. and less are sufficient.

The alkali compounds may be added to

[Pric

the metals used as catalysts before or after or even during the sintering. For example metallic iron which has been obtained by decomposition of iron carbonyl may be mixed in the moistened state with solid potassium chloride before the sintering. Iron compounds, such as oxides or hydroxides, may also have sodium bromide added thereto before their reduction to metallic iron. In many cases it is advantageous to bring the alkali compounds in aqueous solution onto the metal or the metal compound to be reduced.

The metal powders or porous metals may have added to them, in addition to the said alkali compounds, other substances for the purpose of increasing their activity, as for example, the oxides or hydroxides of aluminium, silicon dioxide, kieselguhr, compounds of copper, titanium, manganese, tungsten, molybdenum, chromium, thorium, cerium, zirconium or other rare earths.

The reaction of carbon monoxide and hydrogen may be carried out in the gas phase or in the presence of a liquid medium in the liquid phase. In the latter case there is preferably used as the liquid medium liquid or fusible hydrocarbons, as for example mineral oils or their fractions, tar oils, destructive hydrogenation products or paraffin wax, and especially advantageously oils which have been obtained by the reaction of carbon monoxide and hydrogen, preferably under the same conditions.

The initial gases, carbon monoxide and hydrogen, may be used in the same proportions by volume, but more carbon monoxide than hydrogen or more hydrogen than carbon monoxide may also be present. Additional amounts of carbon monoxide or hydrogen or both gases may also be added at different parts of the reaction vessel. In many cases it is advantageous to react gas mixtures having more than 50 per cent., as for example from 60 to 70 per cent., of carbon monoxide.

The reaction of the carbon monoxide and hydrogen is advantageously carried out at temperatures between about 180° and 450° Centigrade and preferably at increased pressures, such for examples as 5, 10, 20, 50, 100 atmospheres or more. Atmospheric pressure may, however, also be used.

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

EXAMPLE.

Iron powder which has been obtained by thermal decomposition or iron carbonyl is made into a paste with 5 per cent. by weight of potassium chloride stirred into the same weight of water, then heated, pressed into pills of the size of peas and then treated for 4 hours with hydrogen at 850° Centigrade. The catalyst thus obtained is charged into a reaction vessel into which a gas mixture of 35 per cent. of carbon monoxide, 64 per cent. of hydrogen and 1 per cent. of nitrogen is led at 330° Centigrade under a pressure of 15 atmospheres. A liquid product is thus formed of which a few per cent. consists of oxygen-containing derivatives of hydrocarbons and of which about 95 per cent. boils in the boiling range of benzine.

Dated this 21st day of September, 1937.

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

COMPLETE SPECIFICATION.

Improvements in Reacting Carbon Monoxide with 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:—

It is already known from British Specifications Nos. 474,448, 490,090 and 496,880 to carry out the conversion of carbon monoxide and hydrogen in the presence of sintered metals of the iron group as catalysts; it is also known from Specification No. 312,717 to carry out the said conversion in the presence of a metal of the iron group, which, however, has not been sintered, and an alkali metal compound.

My foreign correspondents have found that by the reaction of carbon monoxide with hydrogen at elevated temperatures, valuable hydrocarbon products and contingently oxygen containing derivatives of hydrocarbons, in particular low boiling hydrocarbons of the boiling range of benzines and heavy benzines are obtained by using catalysts consisting wholly or mainly of sintered metals of the iron group to which there are added alkali compounds which in aqueous solution have a neutral or acid reaction and which are practically undecomposed at temperatures up to 1000° Centigrade.

The sintered metals of the iron group, of which iron is preferably employed, may be prepared in particular from metal powders or porous metals.

The metal powders may be prepared in any suitable way, as for example by decomposition of organic-metallic compounds, such as iron carbonyl, or by reduction of pulverulent metal oxides or hydroxides or by the decomposition and reduction of other suitable metal compounds, such as carbonates, nitrates, or oxalates.

Porous metals suitable for sintering can be prepared by reduction of pieces of metal oxides or hydroxides or by pressing metal powders, as for example pulverulent carbonyl iron.

The sintering of the metals is effected by heating to temperatures above 500° Centigrade, advantageously above 600° Centigrade, as for example at 700°, 800°, 900° or 1000° Centigrade, in such a manner, i.e. for so long a time, that a visible decrease in volume (preferably more than 10 per cent.) takes place; in the case of metal powders the powder particles agglomerate and in the case of porous metals there is a decrease in porosity. Non-oxidising gases, such as nitrogen, may be present during the sintering. In many cases it is advantageous to work in the presence of reducing gases, such as hydrogen or gases containing hydrogen. The sintering may also be carried out *in vacuo*. When starting from reducible metal compounds, these may first be converted into the metals by treatment at relatively low temperatures, as for example at from 400° to 500° Centigrade, with reducing gases, whereby no sintering takes place, and then sintered at above 500°, advantageously above 600° Centigrade in the presence of non-oxidising gases or *in vacuo*. The reduction and sintering may, however, also be effected in one single operation, for example by treating an oxide at temperatures above 500° (as for example 850°) Centigrade with reducing gases for such a length of time that not only a reduction but also a sintering of the metal formed by the reduction takes place. The speed of flow and the partial pressure of the hydrogen should be adapted to the speed of reduction of the metal compound treated.

The sintering may also be effected in different stages of pressure, for example by first working at atmospheric pressure and then, at the same or a different temperature, under superatmospheric pressure, as for example at 2, 5, 10, 50, 100 atmospheres or more. The sintering in one stage may also be effected under superatmospheric pressure.

As alkali compounds to be added there may be mentioned in particular alkali halides, as for example potassium chloride, potassium bromide, sodium chloride, or sodium fluoride. Other alkali compounds according to the process of the present invention are, for example the non-alkaline reacting phosphates of sodium and potassium, such as monosodium phosphate and monopotassium phosphate. Generally speaking the said alkali compounds are added in an amount of 0.5, 2, 5, 10, 15 per cent. by weight or more (with reference to the metal used). In many cases, additions of 0.1 per cent. and less are sufficient.

The alkali compounds may be added to the metals used as catalysts before or after or even during the sintering. For example metallic iron which has been obtained by decomposition of iron carbonyl may be mixed in the moistened state with solid potassium chloride before the sintering. Iron compounds, such as oxides or hydroxides, may also have sodium bromide added thereto before their reduction to metallic iron. In many cases it is advantageous to bring the alkali compounds in aqueous solution onto the metal or the metal compound to be reduced.

The metal powders or porous metals may have added to them, in addition to the said alkali compounds, other substances for the purpose of increasing their activity, as for example the oxide or hydroxide of aluminium, silicon dioxide, kieselguhr, compounds of copper, titanium, manganese, tungsten, molybdenum, chromium, thorium, cerium, zirconium or other rare earths. The said substances are added only in such minor proportions that the metal of the iron group forms the main constituent of the catalyst.

The reaction of carbon monoxide and hydrogen may be carried out in the gas phase or in the presence of a liquid medium in the liquid phase. In the latter case there is preferably used as the liquid medium liquid or fusible hydrocarbons, as for example mineral oils or their fractions, tar oils, paraffin wax, destructive hydrogenation products of carbonaceous materials, and especially advantageously oils which have been obtained by the reaction of carbon monoxide and hydrogen, preferably under the same conditions.

The initial gases, carbon monoxide and hydrogen, may be used in the same proportions by volume, but more carbon monoxide than hydrogen or more hydrogen than carbon monoxide may also be present. Additional amounts of carbon monoxide or hydrogen or both gases may also be added at different parts of the reaction vessel. In many cases it is advantageous to react gas mixtures having more than 50 per cent. as for example from 60 to 70 per cent., of carbon monoxide.

The reaction of the carbon monoxide and hydrogen is advantageously carried out at temperatures between about 180° and 450° Centigrade and preferably at increased pressures, such for example as 5, 10, 20, 50, 100 atmospheres or more. Atmospheric pressure may, however, also be used. The reaction products are mainly low boiling hydrocarbons of the boiling range of benzines and heavy benzines, but also other hydrocarbons are formed, such as those boiling in the boiling range of middle oil and heavy oil, as well as paraffin wax and gaseous hydrocarbons, containing more than one carbon atom in the molecule, and also liquid oxygen derivatives of hydrocarbons, as for example methanol or higher alcohols, such as isobutyl alcohol, or ketones, aldehydes or acids are formed to a smaller or larger extent depending upon the particular reaction conditions maintained.

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.

Iron powder which has been obtained by thermal decomposition or iron carbonyl is made into a paste with 5 per cent. by weight of potassium chloride stirred into the same weight of water, then heated, pressed into pills of the size of peas and then treated for 4 hours with hydrogen at 850° Centigrade whereby sintering occurs. The catalyst thus obtained is charged into a reaction vessel into which a gas mixture of 35 per cent. of carbon monoxide, 64 per cent. of hydrogen and 1 per cent. of nitrogen is led at 330° Centigrade under a pressure of 15 atmospheres. A liquid product is thus formed which consists mainly of hydrocarbons with a few per cent. of oxygen-containing derivatives of hydrocarbons and of which about 95 per cent. boils in the boiling range of benzine.

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 production of valuable hydrocarbon products and contingently oxygen containing derivatives of hydrocarbons by reacting carbon monoxide with hydrogen, at elevated temperatures, in the presence of a catalyst consisting wholly or mainly of a sintered metal of the iron group to which is added an alkali compound which in aqueous solution has a neutral or acid reaction and which is practically undecomposed at temperatures up to 1000° Centigrade.

2. In the process as claimed in claim 1, the use of sintered iron.

3. A process as claimed in claim 1 or 2, in which the alkali compound is an alkali halide.

4. The process for the production of valuable hydrocarbon products and oxygen containing derivatives of hydrocarbons substantially as described in the foregoing Example.

5. Valuable hydrocarbon products as herein described when obtained by the process particularly described and ascertained.

Dated this 22nd day of August, 1938.

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

Abingdon : Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 8138.—50/9/1939.]