PATENT SPECIFICATION

Application Date: May 18, 1928. No. 14,639 / 28.

317,808

Complete Left: Feb. 2, 1929.

Complete Accepted: Aug. 19, 1929.

1192

PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Organic Compounds from Oxides of Carbon and Hydrogen.

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:—

It is already known that organic products containing oxygen as well as such as are free from the latter, may be obtained from oxides of carbon and from hydrogen or gases rich in hydrogen, for example methane, by catalytic reaction. A large variety of catalysts suitable for this purpose have already been described as well as such as contain the elements of the iron group.

Difficulties are however encountered when working with catalysts containing the elements of the 8th group, especially when using large quantities of catalysts and when working under pressure, since very often the desired reaction does not take place but leads very considerably to the formation of methane and to the deposition of carbon.

Moreover, it is known, that such difficulties as the evolution of methane and the deposition of carbon may be avoided, in effecting the treatment with catalysts, containing besides copper, silver, gold, which are elements of the first sub-group of the periodic system, singly or as mixtures or alloys, small quantities of other elements, especially those of the iron group, or compounds thereof, and substantially in the absence of carriers of low heat conductivity.

My foreign correspondents have now found that when using catalysts containing substantial amounts of elements of the 8th group, preferably iron, cobalt, or nickel, singly or together with other additions, the said elements may be used even in such quantities as exceed the amount of the fist-named metals, in so far as gaseous mixtures are employed, at pressures of more than 20 atmospheres in which the proportion of hydrogen or methane or of another gas, rich in hydrogen exceeds that of the carbon monoxide. In such a case it is also possible to operate in the presence of carriers of low heat conductivity. These catalysts may also contain elements forming difficultly reducible oxides, such as zinc, magnesium, aluminium, chromium, molybdenum, tungsten, uranium, manganese and the like or compounds thereof, in small amounts not exceeding 5 per cent. The presence of alkali metals in the catalysts is of special advantage. Quantities of 1 per cent. or even still less are sufficient to increase the activity of the catalysts very considerably.

The catalysts may be prepared in many different ways. Thus they may be prepared from the oxides by carefully heating the nitrates, but the components concerned can also be precipitated jointly, from solutions in the form of hydroxides, carbonates or the like, if necessary in the presence of a carrier such as asbestos, pumice or the like followed by a good washing; moreover, the oxides or hydroxides and the like may be intimately mixed and then introduced into the contact chamber after previous reduction if required. Very efficient and usually highly porous catalysts are obtained by using ferrous- and ferricyanides. If oxides of carbon are present in a greater amount than 25 per cent of the hydrogen contained in the gaseous mixture, the catalysts must be free from cadmium or thallium.

Operation with catalysts of the described composition leads under suitable conditions of reaction, besides the formation of valuable gaseous, liquid, and solid hydrocarbons, to larger or smaller quantities of products containing oxygen, such as alcohols, acids, esters, ketones, fats and the like. Especially when working at temperatures below 320° Centigrade, a considerable amount of ethyl alcohol, besides other organic reaction products is formed.

Besides ethyl alcohol, varying quantities of methyl alcohol, higher alcohols and of the products already mentioned, are generally formed. The separation of the ethyl alcohol from the reaction products is very simple, since the reaction

[Price

P.

products usually separate into two layers; the upper one containing hydrocarbons besides higher alcohols and the like, the lower one ethyl alcohol, and small amounts of higher alcohols. The production of alcohols other than ethyl alcohol, and also of the hydrocarbons, may be extensively reduced by a suitable choice of the working conditions and the catalysts. Conversely, when larger proportions of benzine in relation to ethyl alcohol are desired, the yield of the former may be increased, for example, by the addition of substances to the catalyst capable of splitting off water, by means of which the alcohol formed is dehydrated to liquid hydrocarbons, through the stage of ethylene. The methods known for building up of compounds from gases by catalysis, especially from carbon monoxide and hydrogen, such as operating, in a cycle, the preliminary purification of the gases, the separation of the reaction products by cooling and/or by adsorbent masses and the like may naturally also be applied in the process according to this invention.

The starting materials may consist of the most diverse gaseous mixtures, such as water gas, producer gas, or mixtures thereof and may, if necessary be provided with an addition of carbon monoxide or hydrogen or other gases. Yet hydrocarbons or tar oils and the like may be subjected to incomplete combustion with oxygen or mixtures of oxygen and steam, and the resulting gases may be employed after purification and, when desirable, after parts of the carbon monoxide has been catalytically converted by means of steam. The relative proportions in which the carbon oxides and hydrogen or hydrocarbons rich in hydrogen may be present in the reaction gases, may vary within wide limits. Yet it is of particular advantage to employ gaseous mixtures, containing in proportion of oxides of carbon, which is less than 25 per cent of the hydrogen present.

On lowering the pressure, the amount of compounds containing oxygen comprised in the reaction product is diminished and finally at ordinary pressure the amount thereof is nil or only very small. The products containing oxygen consist among others to a large degree of esters boiling between 150° to 300°, which are very suitable for use as solvents or as plasticising agents.

Very valuable fats and waxes may be recovered from the fractions of high boiling point range. The liquid hydrocarbons and the alcohols may be employed as engine fuels. The gaseous reaction products may be extracted from the gases by strong cooling, adsorption with active charcoal or by washing with wash oils and, if desired, may be converted by further treatment, into alcohols or even into liquid hydrocarbons. They may also be used as illuminating or heating gases and the like.

The following Examples will further illustrate the nature of the invention but the invention is not restricted to the Examples. The parts are by weight.

EXAMPLE 1.

1 part of ferric nitrate, 2 parts of cupric nitrate and 0.1 part of potassium carbonate are depositied on 10 parts of pumice stone, by evaporating their concentrated solution, and the nitrates are decomposed by a brief calcination. This catalyst is reduced in a tube at 300° Centigrade for 10 hours, at ordinary pressure, in a current of hydrogen, whereupon a mixture of 32 per cent of carbon monoxide, 64 per cent of hydrogen and 4 per cent of nitrogen is passed over it in the same tube at 200 atmospheres and at 350° Centigrade. The reaction gases deposit an oil containing higher hydrocarbons, alcohols and esters and also an aqueous condensate containing lower alcohols and fatty acids. Considerable quantities of hydrocarbons of the benzine type are recovered from the residual gases by adsorption with charcoal. The catalyst retains its activity for a long period without any appreciable amount of carbon being deposited.

EXAMPLE 2.

4 parts of ferric nitrate and 1 part of cupric nitrate are dissolved in water, and precipitated with a 10 per cent solution of potassium carbonate. The precipitate is filtered by suction, washed several times and dried at 150° Centigrade, Exhaustive washing is undesirable, the presence of small quantities of residual alkali being beneficial.

Over this catalyst, which may also be distributed on pumice, a mixture of 32 per cent of carbon monoxide, 64 per cent of hydrogen and 4 per cent of nitrogen is passed in circulation, under the conditions specified in Example 1. In this case also, the residual gases deposit an oil containing higher hydrocarbons, alcohols and esters, and an aqueous condensate containing lower alcohols and fatty acids. Abundant quantities of hydrocarbons of the benzine type are further extracted from the residual gases by means of adsorption with charcoal. The contact retains its activity for a long period, without any appreciable contamination with deposited carbon.

Similar results are obtained, according to both the preceding Examples, on substituting carbon dioxide for the carbon monoxide.

EXAMPLE 3.

A solution which contains 12 parts of iron, 2 parts of zinc and 12 parts of copper, in the form of their nitrates is precipitated with potassium carbonate, the resulting precipitate being extensively washed and dried. About 3 litres of the resulting catalyst are charged into a copper-lined catalyst tube, a gaseous mixture containing 20 per cent of carbon monoxide, 8 per cent of methane, 70 per cent of hydrogen and 2 per cent of nitrogen (freed from carbon dioxide and sulphur compounds in the usual manner) being then passed, at the rate of 4 cubic metres per hour, over the catalyst at a temperature of 240° Centigrade and under a pressure of 300 atmospheres. On cooling the reaction gases in a pressure separator, cooled to ordinary temperature, a liquid is obtained which consists of two layers, the upper one consisting chiefly of hydrocarbons, whilst the lower one contains about 30 to 40 per cent of ethyl alcohol, together with water. The catalyst may be employed for a long time without losing its efficiency.

By interposing a vessel charged with active charcoal in the rear of the separator, benzines may be recovered from the reaction gases by means of adsorption.

In a single passage over the catalyst, the whole of the carbon monoxide is converted into organic products. After addition of a suitable amount of water-gas, the remaining gas is again passed over the catalyst by means of a circulation pump.

Dated this 18th day of May, 1928.

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

COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Organic Compounds from Oxides of Carbon and Hydrogen.

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 valuable organic compounds, in particular such as contain oxygen, for example alcohols such as ethyl alcohol and methanol, acids, esters, ketones, fats and the like and also hydrocarbons.

It is already known that organic products containing oxygen as well as those which are free from the latter, may be obtained from oxides of carbon and from hydrogen or gases rich in hydrogen, for example methane, by catalytic reaction. A large variety of catalysts suitable for this purpose have already been described, as well as such as contain the elements of the iron group. Thus the production of organic compounds containing oxygen, either alone or in conjunction with hydrocarbons has been proposed by the reduction of oxides of carbon with hydrogen under diminished, ordinary or slightly elevated pressure of up to about 20 atmospheres and at an elevated temperature while operating at temperatures below 300° Centigrade and employing a catalyst consisting of iron with small additions of oxides or hydroxides of the alkali metals or alkaline earths, the said catalyst being used alone or in conjunction with other substances. As an example of a catalyst suitable for application in the said process is mentioned a catalyst obtained by producing a precipitate from an aqueous solution containing ferric nitrate and cupric nitrate in the molecular ratio 2 : 1 by means of dilute caustic soda solution and washing the precipitate thus obtained until it is free from nitrate and still contains 0.32 per cent of sodium hydroxide, when dried, the said catalyst being then reduced with hydrogen for 64 hours at 350° Centigrade. It has further been proposed in Specification No. 2306 A.D. 1914 to hydrogenise carbon compounds, including the oxides of carbon, by treatment with hydrogen in the presence of a catalytic agent consisting of an intimate mixture of either iron, nickel, cobalt or copper with a compound containing-oxygen characterized by being or containing or giving rise to high melting and difficultly reducible oxides or oxygen compounds of weak basic or neutral or acid character, tungstates and selenates of the alkaline earth and of lithium being mentioned as examples of such compounds.

Difficulties are however encountered

when working with catalysts containing the elements of the 8th group, especially when using large quantities of catalysts and when working under pressure, since very often the desired reaction does not take place but leads to a considerable extent to the formation of methane and to the deposition of carbon.

Moreover, it is known, that such difficulties as the evolution of methane and the deposition of carbon may be avoided, in effecting the treatment with catalysts, containing besides copper, silver, gold, which are elements of the first sub-group of the periodic system, singly or as mixtures or alloys, small quantities of other elements, especially those of the iron group, or compounds thereof, and substantially in the absence of carriers of low heat conductivity.

My foreign correspondents have now found that when using catalysts of the aforesaid character substantial amounts, even amounts exceeding the quantity of copper, silver or gold may be present of elements of the 8th group, preferably iron-cobalt or nickel, singly or together with other additions, provided that gaseous mixtures are employed, at pressures of more than 20 atmospheres in which the proportion of hydrogen or methane or other gas rich in hydrogen, exceeds that of the carbon monoxide. In such a case it is possible also to operate in the presence of carriers of low heat conductivity. These catalysts may also contain elements forming difficultly reducible oxides, such as zinc, magnesium, aluminium, chromium, molybdenum, tungsten, uranium, manganese, and the like or compounds thereof, in small amounts not exceeding 5 per cent. The presence of alkali metals in the catalyst is of special advantage. Quantities of 1 per cent or even still less are sufficient to increase the activity of the catalysts very considerably.

The catalysts may be prepared in many different ways. Thus they may be prepared from the oxides by carefully heating the nitrates, but the components concerned can also be precipitated jointly, from solutions in the form of hydroxides, carbonates or the like, if necessary in the presence of a carrier such as asbestos, pumice, or the like, followed by a good washing; moreover, the oxides or hydroxides and the like may be intimately mixed and then introduced into the contact chamber after previous reduction if required. Very efficient and usually highly porous catalysts are obtained by using ferrocyanides and ferricyanides. If oxides of carbon are present in a greater amount than 25 per cent of the hydrogen contained in the gaseous mixture, the catalysts must however be free from cadmium or thallium.

Operation with catalysts of the described composition leads under suitable conditions of reaction, besides the formation of valuable gaseous, liquid, and solid hydrocarbons, to larger or smaller quantities of products containing oxygen, such as alcohols, acids, esters, detones, fats and the like. Especially when working at temperatures below 320° Centigrade, a considerable amount of ethyl alcohol, besides other organic reaction products is formed.

Besides ethyl alcohol, varying quantities of methyl alcohol, higher alcohols and of the products already mentioned, are generally formed. The separation of the ethyl alcohol from the reaction products is very simple, since the reaction products usually separate into two layers, the upper one containing hydrocarbons besides higher alcohols and the like, the lower one ethyl alcohol, and small amounts of higher alcohols. The production of alcohols other than ethyl alcohol, and also of the hydrocarbons, may be extensively reduced by a suitable choice of the working conditions and the catalysts. Conversely, when larger proportions of benzine in relation to ethyl alcohol are desired, the yield of the former may be increased, for example, by addition of substances to the catalyst capable of splitting off water, by means of which the alcohol formed is dehydrated to liquid hydrocarbons, through the stage of ethylene. The methods known for building up compounds from gases by catalysts, especially from carbon monoxide and hydrogen such as operating in a cycle, the preliminary purification of the gases, the separation of the reaction products by cooling and/or by adsorbent masses and the like may naturally also be applied in the process according to this invention.

The starting materials may consist of the most diverse gaseous mixtures, such as water gas, producer gas, or mixtures thereof and may, if necessary be provided with an addition of carbon monoxide or hydrogen or other gases. Yet hydrocarbons or tar oils and the like may be subjected to incomplete combustion with oxygen or mixtures of oxygen and steam, and the resulting gases may be employed after purification and, when desirable, after part of the carbon monoxide has been catalytically converted by means of steam. The relative proportions in which the carbon oxides and hydrogen or hydrocarbons rich in hydrogen may be present in the reaction gases, may vary within wile limits. Yet it is of particular advantage to employ gaseous mixtures, containing a proportion of oxides of carbon which is less than 25 per cent of the hydrogen present, cadmium or thallium bein present in the catalyst if desired.

On lowering the pressure, the amount of compounds containing oxygen comprised in the reaction product is diminished and finally at ordinary pressure the amount thereof is nil or only very small. The products containing oxygen consist among others to a large degree of esters boiling between 150° to 300° Centigrade, which are very suitable for use as solvents or as plasticising agents.

Very valuable fats and waxes may be recovered from the fractions of high boiling point range. The liquid hydrocarbons and the alcohols may be employed as engine fuels. The gaseous reaction products may be extracted from the gases by strong cooling, absorption with active charcoal or by washing with wash oils and, if desired, may be converted by further treatment, into alcohols or even into liquid hydrocarbons. They may also be used as illuminating or heating gases and the like.

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 by weight.

EXAMPLE 1.

1 part of ferric nitrate, 2 parts of cupric nitrate and 0.1 part of potassium carbonate are deposited on 10 parts of pumice stone, by evaporating their concentrated solution, and the nitrates are decomposed by a brief calcination. This catalyst is reduced in a tube at 300° Centigrade for 10 hours, at ordinary pressure, in a current of hydrogen, whereupon a mixture of 32 per cent of carbon monoxide, 64 per cent of hydrogen and 4 per cent of nitrogen is passed over it in the same tube at 200 atmospheres and at 350° Centigrade. The reaction gases deposit an oil containing higher hydrocarbons, alcohols and esters, and also an aqueous condensate containing lower alcohols and fatty acids. Considerable quantities of hydrocarbons of the benzine tupe are recovered from the residual gases by adsorption with charcoal. The catalyst retains its activity for a long period of time without any appreciable amount of carbon being deposited.

EXAMPLE 2.

4 parts of ferric nitrate and 1 part of cupric nitrate are dissolved in water, and precipitated with a 10 per cent solution of potassium carbonate. The precipitate is filtered by suction, washed several times and dried at 150° Centigrade. Exhaustive washing is undesirable, the presence of small quantities of residual alkali being beneficial.

Over this catalyst, which may also be distributed on pumice, a mixture of 32 per cent of carbon monoxide, 64 per cent of hydrogen and 4 per cent of nitrogen is passed in circulation, under the conditions specified in Example 1. In this case also, the residual gases deposit an oil containing higher hydrocarbons, alcohols and esters, and an aqueous condensate containing lower alcohols and fatty acids. Abundant quantities of hydrocarbons of the benzine type are further extracted from the residual gases by means of adsorption with charcoal. The catalyst retains its activity for a long period of time, without any appreciable contamination with deposited carbon.

Similar results are obtained, according to both the preceding Examples, on substituting carbon dioxide for the carbon monoxide.

EXAMPLE 3.

A solution which contains 12 parts of iron, 2 parts of zinc and 12 parts of copper in the form of their nitrates is precipitated with potassium carbonate, the resulting precipitate being extensively washed and dried. About 3 litres of the resulting catalyst are charged into a copper-lined catalyst tube, a gaseous mixture containing 20 per cent of carbon monoxide, 8 per cent of methane, 70 of hydrogen and 2 per cent of nitrogen, freed from carbon dioxide and sulphur compounds in usual manner, being then passed, at the rate of 4 cubic metres per hour, over the catalyst at a temperature of 240° Centigrade and under a pressure of 300 atmospheres. On cooling the reaction gases in a pressure separator, cooled to ordinary temperature, a liquid is obtained which consists of two layers, the upper one consisting chiefly of hydrocarbons, whilst the lower one contains about 30 to 40 per cent of ethyl alcohol, together with water. The catalyst may be employed for a long time without losing its efficiency.

By interposing a vessel charged with adsorbing charcoal in rear of the separator, benzines may be recovered from the reaction gases.

In a single passage over the catalyst, the whole of the carbon monoxide is converted into organic products. After addition of a suitable amount of watergas, the remaining gas is again passed over the catalyst by means of a circulation pump.

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 Specification No. 300,294 and do not claim anything claimed therein, but what I claim is:—

1. A process for the production of valuable organic compounds from oxides of carbon and hydrogen, which consists in treating gaseous mixtures comprising oxides of carbon and an amount of hydrogen or a gas rich in hydrogen greater than that of the carbon monoxide present at a pressure of more than 20 atmospheres with a catalyst which comprises a mixture of an element from the first sub-group of the periodic system and a large amount of an element from the eighth group of the periodic system and preferably from the iron group, if desired with an addition of less than 5 per cent of a metal forming a difficultly reducible oxide, the said catalyst being free from cadmium and thallium if said gaseous mixture contains oxides of carbon in an amount exceeding 25 per cent of the amount of hydrogen present.

2. In carrying out the process according to claim 1, employing an amount of an element from the eighth group of the periodic system greater than that of the elements from the first sub-group of the periodic system.

3. In carrying out the process as claimed in claims 1 and 2 operating at temperatures below 320° Centigrade.

4. A modification of the process as claimed in claims 1, 2 or 3 which consists in operating with gaseous mixtures containing a proportion of oxides of carbon, which is less than 25 per cent of the hydrogen present, cadmium or thallium being present in the catalyst if desired.

5. The process for the production of valuable organic compounds, substantially as described in each of the foregoing Examples.

6. Valuable organic compounds, when obtained according to the preceding claiming clauses.

Dated this 2nd day of February, 1929.

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. 51A.—125/10/1929.]