[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Hydrocarbons.

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 various hydrocarbons and other organic compounds can be obtained by treating oxides of carbon with hydrogen, or gases rich in hydrogen such as methane, at an elevated temperature and under suitable pressures, in the presence of catalysts. A large number of catalysts have already been proposed, especially activated iron, nickel and cobalt. It is already known that it is advantageous, according to the said process, to add alkalis to the catalysts (see Letters Patent No. 20488 A.D. 1913 and No. 2306 A.D. 1914).

My foreign correspondents have now found that, in order to obtain, according to the said process, continuous high yields of hydrocarbons with more than one carbon atom, especially liquid hydrocarbons, it is a matter of decisive importance that the catalysts employed should contain in addition to a metal of group 8 of the periodic system, a definite quantity of alkali compounds, namely less than about 0.6, and preferably between 0.4 and 0.6 part by weight of alkali, reckoned as alkali metal, per 100 parts by weight of the metal of the 8th group of the periodic system. In order to obtain good yields, it is also essential that the metals should be employed in a finely divided state and not in compact metallic form.

The catalysts may be prepared in a great variety of ways. Ferric oxide, which is completely free from alkali, precipitated, for example, with ammonia, may be employed, the suitable amount of an alkali compound being subsequently added. Again, metals of group 8 may be precipitated by alkalis, and the precipitates washed until the requisite proportion of alkali is contained therein. Moreover, the very finely divided metals, obtained for example by decomposing metal carbonyls, may be activated with suitable amounts of dilute solutions of alkali compounds. The metals of group 8 may be employed singly or mixed together, and also, if desired, in conjunction with other substances such as copper, silver, gold, oxides of the alkaline earths, and the like. The alkali metal compounds may be employed in a great variety of forms, such as hydroxides, carbonates, nitrates, chlorides, ferrocyanides, formates, acetates, oxalates, and the like.

The methods of working already known in the catalytic production of compounds from gases, particularly from carbon monoxide and hydrogen, such for example as working in a cycle, the preliminary purification of the gases, the employment of preliminary catalysts arranged in front of the main catalyst, devices for removing the heat of the reaction, the separation of the reaction products by washing, cooling or with adsorption masses, purifying the circulating gases and the like methods may also be employed according to the present invention. Furthermore, the portions of the apparatus which become heated during the process and come into contact with the gases, may be constructed of silver, copper, manganese bronze, chromium nickel, aluminium, iron alloys such as chromium, tungsten or manganese steels, ferrosilicon or the like, or of iron which is provided with a coating adapted to resist the action of the gases and in particular of carbon monoxide.

A great variety of mixtures containing hydrogen, oxides of carbon and the like may be employed as the initial materials, as for example water gas, coke over gas, coal gas, producer gas, or mixtures of the same, with, if desired, the addition of carbon monoxide, hydrogen or other gases. The relative proportions in which the oxides of carbon on the one hand, and the hydrogen or/and hydrocarbons rich in hydrogen on the other, may exist in the gaseous mixture, may vary considerably. For example, equal volumes of hydrogen and the oxides of carbon may be present in the gases, or the proportions of the oxides of carbon may be higher or lower. In some cases it is

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specially advantageous to employ gaseous mixtures in which the oxides of carbon constitute less than 25 per cent of the hydrogen and/or hydrocarbons rich in hydrogen present. In this case the reaction proceeds with particular ease.

The pressure to be applied may vary within wide limits, and therefore the work may be conducted at ordinary pressure, medium pressures and also very high presures such as 1000 atmospheres and more. The reaction space may be smaller in proportion as the pressure is higher. The deposition of the reaction products occurs with particular ease at elevated pressures. Generally speaking the composition of the reaction product varies according to the catalyst employed in each case. When the content of the catalyst in alkali is low, the low boiling hydrocarbons preponderate, whilst with a higher limit of alkali content there is generally an increased tendency to the formation of higher molecular products. In some cases the formation of hydrocarbons is accompanied by the formation of oxygen compounds, such for example as substances of wax character, high molecular acids, alcohols and the like. If the alkali content is below about 0.03 part by weight of alkali metal per 100 parts of metal of Group 8 of the periodic system, the yields are lower. If the alkali content exceeds the limit of about 0.6 part by weight of alkali metal per 100 parts by weight of metal of Group 8, the catalyst readily becomes inactive owing to the deposition of solid products on its surface.

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

EXAMPLE 1.

A mixed hydroxide, precipitated with ammonia and containing iron and cobalt in the relative proportions of 4 to 1, is decanted several times, filtered by suction and washed. When dry, the mixture is impregnated with a solution of potassium hydroxide, so as to contain 0.14 part by weight of potassium per 100 parts by weight of the iron metals.

The resulting catalyst is again dried and is then charged into the reaction vessel. With a single passage of 1 cubic metre of a gas containing 25 per cent of CO, 70 per cent of H_2, 4 per cent of N, and 1 per cent of methane, at 250° Centigrade and under a pressure of 150 atmospheres, 10 cubic centimetres of the catalyst furnish 20 cubic centimetres of hydrocarbon (benzine) which is liquid at ordinary temperature. Moreover, by supercooling to about −10° Centigrade, 25 cubic centimetres of liquid hydrocarbons (liquid at ordinary temperature) containing more than 1 carbon atom, can be recovered. A similar effect is produced by a catalyst containing 10 parts of palladium and 0.1 part of potassium per 100 parts of iron.

EXAMPLE 2.

A mixture, precipitated with potassium hydroxide, or potassium carbonate and containing iron, cobalt and uranium in the proportions 4 : 2 : 1, is repeatedly decanted and washed with distilled water until its alkali content amounts to 0.17 part by weight of potassium per 100 parts by weight of the metals of Group 8. The mixture is dried at 200° Centigrade.

100 cubic centimetres of the catalyst prepared in this manner furnish, by a single passage of 1 cubic metre of a gas containing about 35 per cent of CO and 65 per cent of H_2, at a reaction temperature of 270° Centigrade and under atmospheric pressure, 27 cubic centimetres of benzine and 5 cubic centimetres of liquefied gaseous hydrocarbons. The decrease of the alkali content in washing is continuously supervised by drying and analysing samples. If the alkali content of the catalyst amounts to only 0.2 part by weight of potassium, per 100 parts by weight of metals of Group 8, the yield of benzine is only small, whilst with an excessive content of alkali, such as 1.5 parts by weight of potassium per 100 parts by weight of metals of Group 8, the yield of benzine hydrocarbons diminishes in favour of higher molecular products. Moreover, the surface of the catalyst becomes coated with solid substances and the catalyst therefore soon becomes inactive. Similar effects are obtained with the following catalysts,

200 parts of iron, 10 parts of cobalt and 0.2 part of potassium, or

40 parts of iron, 20 parts of cobalt and 10 parts of nickel and 0.54 part of sodium or

50 parts of iron, 10 parts of cobalt and 10 parts of vanadium and 0.06 part of potassium.

EXAMPLE 3.

A mixture of oxides or carbonates, precipitated with caustic alkalis or alkali carbonates and containing iron, cobalt and silver in the proportions 4 : 2 : 1 by weight, is decanted with distilled water as often as possible, well washed, and dried at 200° Centigrade. The product is then finely granulated and is repeatedly well extracted by boiling with distilled water, during several hours. It is again dried at 200° Centigrade and is impregnated with a solution of sufficient potassium carbonate to bring its alkali content to 0.16 part by weight of potassium per 100 parts by weight of metals of the iron group. With a single passage of 1 cubic metre of a gas containing about 25 per cent of CO and about 70 per cent of H_2, 4 per cent of N, and 1 per cent of methane, at 290° Centigrade and under a pressure of 50 atmospheres, 30 cubic centimetres of the above catalyst furnish 24 cubic centimetres of benzine and 18 cubic centimetres of liquefied hydrocarbon gases.

EXAMPLE 4.

A mixture of alkali free, freshly precipitated hydroxides of iron, cobalt and barium, containing the said metals in the proportions of 100 : 10 : 1 by weight, is intimately stirred with a solution of sufficient rubidium hydroxide to introduce 0.18 part by weight of rubidium per 100 parts by weight of the metals of Group 8. If the resulting catalyst be employed under the conditions specified in Example 3, but at 275° Centigrade a single passage of the gaseous mixture furnishes 3 grams of a body resembling paraffin, 17 cubic centimetres of benzine and 5 cubic centimetres of liquefied hydrocarbon gases.

EXAMPLE 5.

The hydroxides of iron and copper, freed from alkali, are intimately mixed in the proportions of 5 gram atoms of iron to 3 gram atoms of copper, the mixture being then dried and impregnated with such a quantity of a solution of potassium hydroxide that the dry catalyst contains 0.51 part by weight of potassium per 100 parts by weight of iron. With a single passage of 1 cubic metre of gas containing about 25 per cent of CO and 75 per cent of H_2, under a pressure of 5 atmospheres and a reaction temperature of 260° Centigrade, 150 cubic centimetres of the above catalyst furnish about 50 cubic centimetres of hydrocarbons with more than 1 carbon atom which are liquid at ordinary temperature, and 5 cubic centimetres of hydrocarbons with more than 1 carbon atom to be liquefied at low temperature.

EXAMPLE 6.

The wet mixture of the hydroxides of iron and cobalt precipitated with ammonia and containing the said metals in the proportions of 4 gram atoms of iron to 1 gram atom of cobalt, is well decanted, filtered by suction, washed, and dried at 150° to 200° Centigrade. The highly porous product is impregnated with a sufficient amount of a solution of sodium carbonate for it to contain, when re-dried, 0.44 part by weight of sodium per 100 parts by weight of metals of Group 8. With a single passage of 1 cubic metre of gas containing about 25 per cent of CO and 75 per cent of H_2, at 270° Centigrade and under ordinary pressure, 200 cubic centimetres of this catalyst furnish 38 cubic centimetres of hydrocarbons liquid at ordinary temperature, and 1.2 litres of gaseous hydrocarbons, both products containing more than 1 atom of carbon in the molecule.

Dated this 10th day of March, 1928.
JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London, W.C. 2,
Agents.

COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Hydrocarbons.

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 improvements in the manufacture and production of hydrocarbons by treating oxides of carbon with hydrogen or gases rich in hydrogen.

It is already known that various hydrocarbons and other organic compounds can be obtained by treating oxides of carbon with hydrogen, or gases rich in hydrogen such as methane, at an elevated temperature and under suitable pressures, in the presence of catalysts. A large number of catalysts have already been proposed, especially activated iron, nickel and cobalt. It is already known that it is advantageous, according to the said process, to add alkalis to the catalysts (see Letters Patent No. 20488 A.D. 1913 and No. 2306 A.D. 1914).

My foreign correspondents have now found that, in order to obtain, according to the said process, continuous high yields of hydrocarbons with more than one carbon atom in the molecule, especially liquid hydrocarbons, it is a matter of decisive importance that the catalyst employed should contain, in addition to a metal of group 8 of the periodic system, in particular a metal of the iron group, an amount of alkali compounds, namely less than about 0.6, and preferably between 0.4 and 0.6 part by weight of alkali, reckoned as alkali metal, per 100 parts by weight of the metal of the 8th group of the periodic system. In order to obtain good yields, it is also essential that the metal should be employed in a finely divided state and not in compact metallic form.

The catalysts may be prepared in a great variety of ways. Ferric oxide, which is completely free from alkali, precipitated, for example, with ammonia, may be employed, the suitable amount of an alkali compound being subsequently added. Again, metals of group 8 may be precipitated by alkalis, and the precipitates washed until the requisite proportion of alkali is contained therein. Moreover, the very finely divided metals, obtained for example by decomposing metal carbonyls, may be activated with suitable amounts of dilute solutions of alkali compounds. The metals of group 8 may be employed singly or mixed together, and also, if desired, in conjunction with other substances such as copper, silver, gold, oxides of the alkaline earths, and the like. The alkali metal compounds may be employed in a great variety of forms, such as hydroxides, carbonates, nitrates, chlorides, ferrocyanides, formates, acetates, oxalates and the like.

As suitable catalysts may be mentioned by way of example those consisting of:

80 parts of iron + 20 parts of cobalt + 0.4 part of potassium

80 parts of iron + 20 parts of cobalt + 0.6 part of sodium

100 parts of iron + 8 parts of magnesium oxide + 0.4 part of cesium.

10 parts of iron + 10 parts of cadmium + 0.5 part of potassium

100 parts of iron + 50 parts of copper + 10 parts of manganese oxide + 0.45 part of sodium.

The catalysts may also be employed deposited on carriers, such as pumice stone, carbon, aluminium shreds, porous copper and the like, or these may be impregnated with solutions of salts of the above metals in particular with organic acids, for example with solutions of iron formate, cobalt acetate or the like.

The methods of working already known in the catalytic synthesis of compounds from gases, particularly from carbon monoxide and hydrogen, such for example as working in a cycle, the preliminary purification of the gases, the employment of preliminary catalysts arranged in front of the main catalyst, devices for removing the heat of the reaction, the separation of the reaction products by washing, cooling or with adsorption masses, purifying the circulating gases and the like methods, may also be employed according to the present invention. Furthermore, the portions of the apparatus which become heated during the process and come into contact with the gases, may be constructed of silver, copper, manganese bronze, chromium nickel, aluminium, iron alloys such as chromium, tungsten or manganese steels, ferrosilicon or the like, or of iron which is provided with a coating adapted to resist the action of the gases and in particular of carbon monoxide.

A great variety of mixtures containing hydrogen, oxides of carbon and the like may be employed as the initial materials, as for example water gas, coke oven gas, coal gas, producer gas, or mixtures of the same, with, if desired, the addition of carbon monoxide, hydrogen or other gases. The relative proportions in which the oxides of carbon on the one hand, and the hydrogen or/and hydrocarbons rich in hydrogen on the other, may exist in the gaseous mixture, may vary considerably. For example, equal volumes of hydrogen and the oxides of carbon may be present in the gases, or the proportions of the oxides of carbon may be higher or lower. In some cases it is specially advantageous to employ gaseous mixtures in which the oxides of carbon constitute less than 25 per cent of the hydrogen and/or hydrocarbons rich in hydrogen present. In this case the reaction proceeds with particular ease.

The temperature employed usually ranges between about 225° and 375° Centigrade and very good results are obtained at temperatures of between about 260° and 280° Centigrade.

The pressure to be applied may vary within wide limits, and therefore the work may be conducted at ordinary pressure, medium pressures, say about 20 or 50 atmospheres, and also very high pressures, such as 100 to 200 or even 1000 atmospheres and more. The reaction space may be smaller in proportion as the pressure is higher. The deposition of the reaction products occurs with particular ease at elevated pressures. Generally speaking the composition of the reaction product varies according to the catalyst employed in each case. When the content of the catalyst in alkali is low, the low boiling hydrocarbons preponderate, whilst with a higher limit of alkali content there is generally an increased tendency to the formation of higher molecular products. In some cases the formation of hydrocarbons is accompanied by the formation of oxygen compounds, such for example as substances of wax character, acids of high molecular weight, alcohols and the like. If the alkali content is below about 0.1 part by weight of alkali metal per 100 parts of metal of group 8 of the periodic system, the yields are lower. If the alkali content exceeds the limit of about 0.6 part by weight of alkali metal per 100 parts by weight of metal of group 8, the catalyst readily becomes inactive owing to the deposition of solid products on its surface.

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.

EXAMPLE 1.

A mixed hydroxide, precipitated with ammonia and containing iron and cobalt in the relative proportions of 4 to 1, is decanted several times, filtered by suction and washed. When dry, the mixture is impregnated with a solution of potassium hydroxide, so as to contain 0.14 part by weight of potassium per 100 parts by weight of the iron metals.

The resulting catalyst is again dried and is then charged into the reaction vessel. With a single passage of 1 cubic metre of a gas containing 25 per cent of CO, 70 per cent of H_2, 4 per cent of N_2 and 1 per cent of methane, at 250° Centigrade and under a pressure of 150 atmospheres, 10 cubic centimetres of the catalyst furnish 20 cubic centimetres of hydrocarbon (benzine) which are liquid at ordinary temperature. Moreover, by cooling to about 10° Centigrade below zero, 25 cubic centimetres of liquid hydrocarbons (liquid at ordinary temperature) containing more than 1 carbon atom, can be recovered. A similar effect is produced by a catalyst containing 10 parts of palladium and 0.1 part of potassium per 100 parts of iron.

EXAMPLE 2.

A mixture, precipitated with potassium hydroxide, or potassium carbonate and containing iron, cobalt and uranium in the proportions 4 : 2 : 1, is repeatedly decanted and washed with distilled water until its alkali content amounts to 0.17 part by weight of potassium per 100 parts by weight of the metals of group 8. The mixture is dried at 200° Centigrade.

100 cubic centimetres of the catalyst prepared in this manner furnish, by a single passage of 1 cubic metre of a gas containing about 35 per cent of CO and 65 per cent of H_2, at a reaction temperature of 270° Centigrade and under atmospheric pressure, 27 cubic centimetres of benzine and 5 cubic centimetres of liquefied gaseous hydrocarbons. For the preparation of the catalyst, the decrease of the alkali content in washing is continuously supervised by drying and analysing samples. If the alkali content of the catalyst amounts to only 0.2 part by weight of potassium, per 100 parts by weight of metals of group 8, the yield of benzine is only small, whilst with an excessive content of alkali, such as 1.5 parts by weight of potassium per 100 parts by weight of metals of group 8, the yield of benzine hydrocarbons diminishes in favour of higher molecular products. Moreover, the surface of the catalyst becomes coated with solid substances and the catalyst therefore soon becomes inactive. Similar effects are obtained with the following catalysts.

200 parts of iron, 10 parts of cobalt and 0.2 part of potassium, or

40 parts of iron, 20 parts of cobalt, 10 parts of nickel and 0.34 part of sodium, or

50 parts of iron, 10 parts of cobalt, 10 parts vanadium and 0.08 part of potassium.

EXAMPLE 3.

A mixture of oxides or carbonates, precipitated with caustic alkalis or alkali carbonates and containing iron, cobalt and silver in the proportions 4 : 2 : 1 by weight, is decanted with distilled water as often as possible, well washed, and dried at 200° Centigrade. The product is then finely granulated and is repeatedly well extracted by boiling with distilled water, during a period of several hours. It is again dried at 200° Centigrade and is impregnated with a solution of sufficient potassium carbonate to bring its alkali content to 0.16 part by weight of potassium per 100 parts by weight of metals of the iron group. With a single passage of 1 cubic metre of a gas containing about 25 per cent of CO and about 70 per cent of H_2, 4 per cent of N_2, and 1 per cent of methane, at about 290° Centigrade and under a pressure of 50 atmospheres, 30 cubic centimetres of the above catalyst furnish 24 cubic centimetres of benzine and 18 cubic centimetres of liquefied hydrocarbon gases.

EXAMPLE 4.

A mixture of alkali free, freshly precipitated hydroxides of iron, cobalt and barium, containing the said metals in the proportions 100 : 10 : 1 by weight, is intimately stirred with a solution of sufficient rubidium hydroxide to introduce 0.18 part by weight of rubidium per 100 parts by weight of the metals of group 8. If the resulting catalyst be employed under the conditions specified in Example 3, but at about 275° Centigrade a single passage of the gaseous mixture furnishes 3 grams of a body resembling paraffin wax, 17 cubic centimetres of benzine and 5 cubic centimetres of liquefied hydrocarbon gases.

EXAMPLE 5.

The hydroxides of iron and copper, freed from alkali, are intimately mixed in the proportions of 5 gram atoms of iron to 3 gram atoms of copper, the mixture being then dried and impregnated with such a quantity of a solution of potassium hydroxide that the dry catalyst contains 0.51 part by weight of potassium per 100 parts by weight of iron. With a single passage of 1 cubic metre of gas containing about 25 per cent of CO and 75 per cent of H_2, under a pressure of about 5 atmospheres and a reaction temperature of about 260° Centigrade, 150 cubic centimetres of the above catalyst furnish about 50 cubic centimetres of hydrocarbons with more than 1 carbon atom which are liquid at ordinary temperature, and 5 cubic centimetres of hydrocarbons with more than 1 carbon atom to be liquefied at low temperature.

EXAMPLE 6.

The wet mixture of the hydroxides of iron and cobalt precipitated with ammonia and containing the said metals in the proportions of 4 gram atoms of iron to 1 gram atom of cobalt, is well decanted, filtered by suction, washed, and dried at 150° to 200° Centigrade. The highly porous product is impregnated with a sufficient amount of a solution of sodium carbonate for it to contain, when re-dried, 0.44 part by weight of sodium per 100 parts by weight of metals of group 8. With a single passage of 1 cubic metre of gas containing about 25 per cent of CO and 75 per cent of H_2, at 270° Centigrade and under ordinary pressure, 200 cubic centimetres of this catalyst furnish 38 cubic centimetres of hydrocarbons liquid at ordinary temperature, and 1.2 litres of gaseous hydrocarbons, both products containing more than 1 atom of carbon in the molecule.

I am aware of Specification No. 280,522 as open to public inspection and do not claim anything described therein.

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. In the production of hydrocarbons with more than one carbon atom in the molecule, especially liquid hydrocarbons, by treating oxides of carbon with hydrogen or gases rich in hydrogen, in carrying out the said treatment in the presence of a catalyst containing in addition to a metal of group 8 of the periodic system an amount of an alkali compound equivalent to less than about 0.6 part and preferably between 0.4 and 0.6 part by weight of alkali reckoned as alkali metal per 100 parts by weight of the metal of the 8th group of the periodic system.

2. The process for the production of hydrocarbons with more than one carbon atom in the molecule, especially liquid hydrocarbons, by treating oxides of carbon with hydrogen or gases rich in hydrogen, substantially as described in each of the foregoing examples.

3. Hydrocarbons with more than one carbon atom in the molecule, when obtained in accordance with the preceding claiming clauses.

Dated this 26th day of November, 1928.

JOHNSONS & WILLCOX,
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