[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Synthetic Organic Compounds.

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 process described in the Specification No. 254,760 discloses the production of organic compounds, containing oxygen, from carbon oxides and hydrogen, or hydrocarbons rich in hydrogen, or mixtures of hydrogen and hydrocarbons, at elevated temperatures and pressures, use being made of contact masses containing iron, nickel or cobalt, or compounds of the same, in such a state of combination that no free iron is formed during the contact operation, the compound form being maintained throughout.

My foreign correspondents have now found that, by the reduction of oxides of carbon organic compounds containing or not containing oxygen may be produced in a highly advantageous manner by employing contact masses which, in addition to iron, nickel or cobalt, or compounds of the same, in any convenient form, contain cadmium, or thallium, or their compounds or mixtures of these substances. Such contact masses are effective at comparatively low temperatures as for example even at from 250° to 300° Centigrade, or lower. Again the admixture of cadmium or thallium or their compounds or mixtures completely prevents any deposition of soot on the contact mass even if the gas under treatment be rich in carbon monoxide. The other elements of the 8th group of the periodic system such as platinum, palladium and the like also give in combination with cadmium or thallium, a similar action to that given by iron, nickel or cobalt. The activity of the contact masses is assisted by still further additions of substances such as copper, gold, silver, cerium, zirconium, aluminium, vanadium, uranium, chromium, molybdenum, tungsten, manganese, alkali metals and alkaline earth metals or compounds of the same.

A typical contact mass suitable according to the present invention is one containing iron, copper and cadmium, employed either as such or with still further additions. The contact masses may be used in a great variety of forms, such for example as alloys, and may also be prepared in a great variety of ways. For example, the oxides prepared by carefully heating the nitrates, may be used as initial materials or the components concerned may be precipitated jointly, from solution, as hydroxides, in some cases in the presence of a carrier such as pumice, asbestos and the like, or the oxides or hydroxides and the like may be intimately mixed together, and then charged into the reaction chamber after having, if so desired, been reduced.

Highly effective contact masses may also be obtained by using the corresponding salts of ferro- or ferri-cyanic acid as initial substances. The process may be carried out at ordinary, elevated or very high pressures and even at 1000 atmospheres and higher. According to the conditions of working as regards temperature, pressure, composition of the gases, contact masses and the like, solid liquid or gaseous hydrocarbons may be produced, or also products containing oxygen, or mixtures of these. In some cases, the products containing oxygen consist to a large extent of ethyl alcohol or of esters, which boil at between 150° and 300° Centigrade, and are highly suitable as solvents and softening agents for lacquers and the like. Highly valuable fats and waxes may be recovered from the fractions of high boiling point. The liquid hydrocarbons may be used as motor fuel. The gaseous products may be separated, for example, by strongly cooling adsorption with active carbon, extraction with washing oils and, if desired, may be converted, by further treatment, into alcohols, or also into liquid hydrocarbons. They may also be employed as lighting or heating gas or the like. The working operations already known in the catalytic produc-

tion of compounds from gases, especially from carbon monoxide and hydrogen, namely operating in a continuous cycle, previously purifying the gases, separating the reaction products by cooling and or by adsorption masses, purifying the circulating gases and so on, and also the devices for carrying off the heat of the reaction and the like may also be applied, in a suitable manner, to the present process.

A great variety of gaseous mixtures may be employed such as water gas, coke-oven gas, coal gas, producer gas, or mixtures of the same, with or without the addition of carbon monoxide and other gases. Moreover, coals or hydrocarbons such as natural gas and the like, or tar oils and the like, may be incompletely burned with oxygen, or mixtures of oxygen and steam, the resulting gases being employed after purification and, if necessary, after catalytic conversion of a portion of the carbon monoxide by means of steam into carbon dioxide and hydrogen.

The hydrogen needed for the reaction may also be generated by the aid of the catalyst itself, by wholly or partially replacing the hydrogen in the initial gases by steam, light hydrocarbons such as methane, or mixtures of the same.

Such parts of the apparatus as grow hot and are exposed to the contact with the reaction gases, are preferably constructed, with a view to preventing the deposition of carbon, in place of iron, of silver, copper, manganese bronze, chromium-nickel, aluminium, iron alloys, such as chromium-, tungsten-, or manganese steels, ferrosilicon or the like, or the said parts may be provided with a suitable coating.

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

EXAMPLE 1.

A solution containing 12 parts of iron, 2 parts of cadmium and 3 parts of copper, in the form of nitrates, is precipitated with potassium carbonate, and the resulting precipitate is thoroughly washed and dried. About 8 cubic centimetres of the resulting contact mass are placed in a copper-lined contact tube, through which 60 litres of water gas, freed from carbon dioxide and sulphur compounds in the usual manner, are then passed, per hour, at from 300° to 350° Centigrade and at 100 atmospheres pressure. The separator, which is cooled to the ordinary temperature, but maintained under pressure, furnishes a liquid composed of two layers, the upper one consisting mainly of hydrocarbons, higher alcohols and esters, whilst the lower one consists mainly of water with about 40 per cent. of lower alcohols, especially ethyl alcohol and organic acids. The contact mass may be kept in use for a long period without losing its efficiency.

By attaching a vessel, charged with active carbon, in rear of the separator, benzines and hydrocarbons boiling below 20° Centigrade, may also be recovered.

EXAMPLE 2.

Water gas is passed, as in Example 1, at from 250° to 300° Centigrade and at from 50 to 100 atmospheres pressure over 8 cubic centimetres of cadmium-copper-ferrocyanide. The yield is still higher than in Example 1.

If the operation be conducted at ordinary pressure, considerably larger quantities of contact materials must be employed in order to obtain the same yield.

Dated this 7th day of July, 1927.

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

COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Synthetic Organic Compounds.

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:—

It has already been suggested to produce methanol or products consisting substantially of methanol by reducing carbon monoxide or dioxide at elevated temperature and pressure in the presence of catalysts containing besides one or more of the following elements, copper,

silver, gold, zinc, cadmium and lead, also titanium, vanadium, chromium, manganese and other cognate elements related to them, namely zirconium, cerium, thorium, niobium, tantalum, molybdenum, tungsten, uranium, or boron, or more than one of these elements or compounds, but the specific class of catalysts described and claimed here which furnish particularly good yields has not been disclosed. It has further been suggested to produce organic compounds containing oxygen either alone or in conjunction with hydrocarbons by the reduction of oxides of carbon with hydrogen under diminished, ordinary or slightly elevated pressure and at an elevated temperature below 300° Centigrade in the presence of a catalyst consisting of iron, with small addition of alkalies or alkaline earths or their compounds, if desired in conjunction with other substances. But the present process is carried out specifically with a catalyst comprising in addition to considerable amounts of iron, nickel or cobalt, or compounds of the same, cadmium or thallium or their compounds or mixtures of these substances.

The process described in the Specification No. 254,760 discloses the production of organic compounds, containing oxygen, from carbon oxides and hydrogen, or hydrocarbons rich in hydrogen, or mixtures of hydrogen and hydrocarbons, at elevated temperatures and pressures, use being made of catalysts containing iron, nickel, or cobalt, or compounds of the same, in such a state of combination that no free iron is formed during the contact operation, the compound form being maintained throughout.

My foreign correspondents have now found that by the reduction of oxides of carbon, organic compounds containing or not containing oxygen are produced in a highly advantageous manner when employing catalysts which, in addition to considerable amounts of iron, nickel or cobalt, or compounds of the same, in any convenient form, contain cadmium or thallium, or their compounds or mixtures of these substances, the said catalysts being free from substantial amounts of metal halides and the treatment being carried out without an addition of alcohols, esters or aldehydes. Such catalysts are effective at comparatively low temperatures, as for example even at from 180° to 200° Centigrade, but preferably the process is carried out between about 250° and 350° Centigrade, though the catalysts may also be used at temperatures of about 400° Centigrade. Again the admixture of cadmium or thallium or their compounds or mixtures completely prevents any deposition of soot on the catalysts, even if the gas under treatment be rich in carbon monoxide. The other elements of the 8th group of the periodic system, such as platinum or palladium, also have in combination with cadmium, or thallium, a similar effect to that of iron, nickel or cobalt and may be employed in place of or in conjunction with these latter elements singly or as mixtures. The activity of the catalysts is assisted by still further additions of substances such as copper, gold, silver, cerium, zirconium, aluminium, vanadium, uranium, chromium, molybdenum, tungsten, manganese, alkali metals and alkaline earth metals or compounds of the same, provided that metal compounds containing oxygen which are difficultly reducible to the metal are not present at all or only in an amount not exceeding 5 per cent., preferably less than 1 per cent. of the catalytically active materials.

A typical catalyst suitable according to the present invention is one containing iron, copper and cadmium, employed either as such or with still further additions especially of oxides or carbonates of the alkali metals in the abovementioned amounts. Thus for instance, a catalyst containing more than 50 per cent. of iron besides copper and cadmium and less than one per cent. of an alkali metal in any convenient form is particularly effective. The catalysts may be used in a great variety of forms, such for example as alloys, and may also be prepared in a great variety of ways. For example, the oxides prepared by carefully heating the nitrates may be used as initial materials or the components concerned may be precipitated jointly, from solution, as hydroxides, in some cases in the presence of a carrier, such as pumice, asbestos and the like, or the oxides or hydroxides and the like may be intimately mixed together, and then charged into the reaction chamber after having been reduced. Highly effective catalysts may also be obtained by using the corresponding salts of ferro- or ferri-cyanic acid as initial substances.

The process may be carried out at ordinary or elevated pressure, e.g. up to about 200 atmospheres, though even very high pressures up to 1000 atmospheres and higher may also be used. According to the conditions of working as regards temperature, pressure, composition of the gases, catalysts and the like, solid, liquid, or gaseous hydrocarbons may be produced, or also products containing oxygen or mixtures of these. In some

cases the products containing oxygen consist to a large extent of ethyl alcohol or of esters, which boil betwen 150° and 300° Centigrade, and are highly suitable as solvents and softening agents for lacquers and the like. Highly valuable fats and waxes may be recovered from the fractions of high boiling point. The liquid hydrocarbons may be used as motor fuel. The gaseous products may be separated, for example by strongly cooling, adsorption with active carbon, extraction with washing oils, and, if desired may be converted, by further treatment, into alcohols, or also into liquid hydrocarbons. They may also be employed as lighting or heating gas or the like. The working operations already known in the catalytic production of compounds from gases, especially from carbon monoxide and hydrogen, namely operating in a continuous cycle, previously purifying the gases, separating the reaction products by cooling and/or by adsorption masses, purifying the circulating gases and so on, and also the devices for carrying off the heat of the reaction and the like may also be applied, in a suitable manner, to the present process.

A great variety of gaseous mixtures may be employed such as water gas, coke-oven gas, coal gas, producer gas, or mixtures of the same, with or without the addition of carbon monoxide and other gases. Moreover, coals or hydrocarbons such as natural gas and the like, or tar oils and the like, may be incompletely burned with oxygen, or mixtures of oxygen and steam, the resulting gases being employed after purification and, if necessary, after catalytic conversion of a portion of the carbon monoxide by means of steam into carbon dioxide and hydrogen.

The hydrogen needed for the reaction may also be generated by the aid of the catalyst itself, by wholly or partially replacing the hydrogen in the initial gases by steam, light hydrocarbons such as methane, or mixtures of the same.

Such parts of the apparatus as grow hot and are exposed to the contact with the reaction gases, are preferably constructed, with a view to preventing the deposition of carbon, in place of iron, of silver, copper, manganese bronze, chromium-nickel, aluminium, iron alloys, such as chromium-, tungsten- or manganese-steels, ferrosilicon or the like, or the said parts may be provided with a suitable coating.

The following examples will further illustrate how the said invention may be carried into practical effect, but the invention is not limited thereto. The parts are by weight.

EXAMPLE 1.

A solution containing 12 parts of iron, 2 parts of cadmium and 3 parts of copper, in the form of nitrates, is precipitated with potassium carbonate, and the resulting precipitate is thoroughly washed and dried. Over the resulting catalyst placed in a copper-lined contact tube, water gas, freed from carbon dioxide and sulphur compounds in the usual manner, is passed at the rate of 60 litres per each 8 cubic centimetres of the catalyst per hour, at from 300° to 350° Centigrade and at 100 atmospheres pressure. From the separator, which is cooled to the ordinary temperature, but maintained under pressure, a liquid is drawn off composed of two layers, the upper one consisting mainly of hydrocarbons, higher alcohols and esters, while the lower one consists mainly of water with about 40 per cent. of lower alcohols, especially ethyl alcohol and organic acids. The catalyst may be kept in use for a long period without losing its efficiency.

By attaching a vessel, charged with active carbon, in rear of the separator, benzines and hydrocarbons boiling below 20° Centigrade, may also be recovered.

EXAMPLE 2.

Water gas is passed, at the rate of flow described in Example 1, at from 250° to 300° Centigrade and at from 50 to 100 atmospheres pressure over cadmium-copper-ferrocyanide prepared by precipitating a solution of potassium ferrocyanide with a solution of cadmium and copper salts. The yield is still higher than in Example 1.

If the operation be conducted at ordinary pressure, considerably larger quantities of catalysts, for example 20 times the amount employed in the foregoing, must be introduced in order to obtain the same yield.

EXAMPLE 3.

A solution of 2 molecular proportions of iron nitrate and 1 molecular proportion each of thallous nitrate and copper nitrate are precipitated with such an amount of sodium carbonate that litmus paper just becomes blue, in the form of their carbonates, and the precipitate thus obtained is decanted, filtered, washed and dried. Under the conditions of working specified in Example 1 ample quantities of hydrocarbons and organic compounds containing oxygen are obtained with the above catalyst which does not gradually lose its efficiency by deposition of carbon as is usually the case when employing iron catalysts free from cadmium or thallium.

A similar action is produced by catalysts prepared by precipitating the heavy metal components from solutions of their salts by means of the calculated amount of ammonia, intimately mixing the precipitates and impregnating them, after drying, with such small amounts of sodium, potassium, or lithium carbonate, that the alkali carbonate content of the catalyst preferably does not exceed 1 per cent. calculated as metal.

A process has already been suggested for the production of a catalyst for the synthesis of oxygenated organic compounds by subjecting mixtures or compounds containing hexavalent chromium and one or more of the catalytic group of metals including zinc, copper, cadmium, magnesium, manganese, silver and iron to a treatment at red heat to form chromites containing trivalent chromium and I make no claim to this process here.

I am aware of Specifications Nos. 229,714 and 237,030 and do not claim anything described or claimed 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. A process for the manufacture and production of synthetic organic compounds which consists in reducing oxides of carbon at elevated temperature and ordinary or elevated pressure in the presence of a catalyst comprising in addition to considerable amounts of iron, nickel or cobalt or compounds of the same cadmium or thallium or their compounds or mixtures of these substances, the said catalysts being free from substantial amounts of metal halides and the treatment being carried out without an addition of alcohols, esters, or aldehydes.

2. A modification of the process according to Claim 1, which consists in employing a catalyst containing, in place of or in conjunction with iron, nickel or cobalt, one or more of the other elements of the group 8 of the periodic system.

3. A specific manner of carrying out the processes according to Claims 1 and 2, which consists in employing a catalyst as defined therein containing additions of other substances such as copper, gold, silver, cerium, zirconium, aluminium, vanadium, uranium, chromium, molybdenum, tungsten, manganese, alkali metals and alkaline earth metals or compounds of the same, provided that metal compounds containing oxygen which are difficultly reducible to the metal should not be present at all or only in an amount not exceeding 5 per cent., preferably less than 1 per cent. of the catalytically active material.

4. A process for the manufacture and production of synthetic organic compounds, substantially as described in each of the foregoing examples.

5. Synthetic organic compounds when prepared in accordance with the preceding claiming clauses.

Dated this 5th day of April, 1928.

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