AMENDED SPECIFICATION.

Reprinted as amended under Section 8 of the Patents and Designs Acts, 1907 and 1919.

78

PATENT SPECIFICATION

254,819

Application Date: March 9, 1925. No. 6883/25.

Complete Accepted: July 9, 1926.

COMPLETE SPECIFICATION (AMENDED).

Improvements in the Synthesis of 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 the Badische Anilin and Soda Fabrik, of Ludwigshafen-on-Rhine, Germany, a corporation organised according to German laws) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It is known that oxides of carbon by reacting with hydrogen under the influence of catalysts can be reduced to methanol with or without oxygenated organic compounds of a higher order. Carbon monoxide has also been brought into reaction with liquid alcohol in the presence of sodium alcoholate by which method alkyl formates have been produced.

My foreign correspondents have now found that valuable organic compounds can also be synthesized by acting on aliphatic alcohols in a vapourised condition with carbon monoxide at an elevated temperature and under elevated pressure and in the presence of catalysts.

Various catalysts may be employed for effecting the desired reaction and in accordance with the invention such contact masses are employed as contain a hydrating constituent. Examples of such constituents are the oxides of titanium, zirconium, thorium, vanadium, niobium, manganese, cerium, lanthanum, tantalum, chromium, molybdenum tungsten, uranium, didymium, glucinium, aluminium and others. An addition of alkali, or alkaline earth metal compounds is often helpful for increasing the hydrating efficiency of the contact masses. The oxides of zinc and cadmium when mixed with caustic alkalies are also suitable as hydrating agents and such mixtures can be used as contact masses for the present purpose. Generally the presence of hydrogenating constituents in conjunction with hydrating constituents alone or with alkali or alkaline earth compounds is very useful, and as examples of such hydrogenating constituents, copper, silver, gold, tin, lead, antimony, bismuth, zinc, cadmium and thallium may be mentioned, or oxides and other compounds of the aforesaid elements. Iron, nickel and cobalt may also be present as suitable hydrogenating catalysts (when as metals) or hydrating catalysts (when as oxides) provided they are used in a combined condition, whether chemically or in the form of alloys. The nature of the products varies, to some degree, in accordance with the special catalyst actually used and the temperature of the reaction. Generally the higher the temperature and the longer the vapours are exposed to the contact mass, the higher boiling products are obtained.

For example when methanol vapour and carbon monoxide are passed over a contact mass containing oxides of iron and manganese at a temperature of about 400 degrees Centigrade and an elevated pressure, a product containing several acids,

[*Price 1/-*]

particularly butyric and valeric acid, free or combined, is obtained.

Other gases, for example, hydrogen, or nitrogen, may also be present in addition to carbon monoxide. In some such cases products containing nitrogen will be formed. For instance, if a mixture of methanol, carbon monoxide, nitrogen and hydrogen is passed at 480 degrees Centigrade and a total pressure of 200 atmospheres, over a contact mass prepared from 8 parts of molybdic acid and 2 parts of cobalt oxide, besides oxygen containing organic compounds, nitrogeneous compounds, such as the amines derived from methyl alcohol are obtained. Similar results are obtained when employing a contact mass prepared from barium uranate or iron vanadate.

The process can, if desired, be carried out in a circulating system, or with several contact vessels, the products formed being separated after each treatment and the residual gases returned into the original catalytic vessel or into one or more subsequent catalytic vessels, after replenishing the gases consumed by the reaction. The cooler for separating the products may be kept at a suitable temperature to effect only condensation of higher boiling products, leaving for example methanol and other materials of low boiling point in a vapour state, and several coolers or receivers, kept at several different temperatures may be arranged to effect direct separation into distinct fractions.

It is not necessary, according to this invention, to employ separated alcohols. For example, the methanol carrying gas mixtures obtained by catalytic treatment of gases containing carbon oxides and hydrogen with the aid of a suitable methanol-forming contact mass may be directly employed and subjected to a second catalytic treatment in which a contact mass as defined above is employed adding, if required, carbon monoxide or hydrogen or mixtures of both. This double treatment is quite different from the method described in the prior Specification No. 238,319 according to which, in a single catalytic treatment, carbon monoxide is converted into methanol with ample quantities of higher alcohols and other compounds containing oxygen, and which single treatment is not claimed here.

Instead of methanol, methyl formate, or a mixture of methanol and methyl formate, or other esters or mixtures of esters and alcohols may be employed. Aldehydes may also be employed, when hydrogen is present, instead of alcohols.

The following examples will serve to illustrate further the manner of carrying this invention into practice, but the invention is not limited to these examples.

Example 1.

A mixture of 10 per cent. by volume of methanol vapour and 90 per cent. by volume of carbon monoxide is passed, at a pressure of 200 atmospheres and at 420 degrees Centigrade over a contact mass prepared from a mixture of 3 parts by weight of potassium chromate and 2 parts by weight of potassium molybdate. On cooling the reaction gases, a product is separated which contains higher alcohols, aldehydes and several aliphatic acids in the form of esters. The temperature of the reaction may be varied, the products possessing generally higher boiling points when obtained at higher temperatures.

Example 2.

A mixture of 10 per cent. by volume of ethyl alcohol vapour and 90 per cent. by volume of carbon monoxide, free from iron carbonyl, is passed, at 400 degrees Centigrade and 200 atmospheres, over a catalyst prepared from a mixture containing 5 parts by weight of zinc oxide, 3 parts by weight of chromium oxide and 3 parts by weight of manganese oxide and placed in a tube lined with copper capable of resisting high pressure. On cooling, oxygenated products are obtained in ample quantities, for a minor part boiling below ethyl alcohol, chiefly, however, at from 100 to 250 degrees Centigrade and higher. Various higher aldehydes, acids and esters thereof are contained in the product, besides ethyl alcohol and higher alcohols and water.

A mixture of methanol and ethanol may also be employed.

Example 3.

A mixture composed of 7 per cent. by volume, of methanol vapour, 20 per cent. of carbon monoxide, 70 per cent. of hydrogen and 3 per cent. of nitrogen is passed, at about 450 degrees Centigrade and 200 atmospheres, over a contact mass prepared from a mixture of 2 parts by weight of potassium bichromate and 1 part by weight zinc oxide. Large quantities of oxygenated organic compounds of a higher molecular nature, both soluble and insoluble in water, are produced. Isobutanol, normal propanol, amyl and higher alcohols and about 10 per cent. of free and combined acids are found therein.

The gaseous mixture mentioned may be obtained by passing a mixture of hydrogen, carbon monoxide and a small amount of nitrogen through methanol, kept at say 160 degrees Centigrade, or through a device down which methanol trickles, or the alcohol may be sprayed into the reaction vessel.

EXAMPLE 4.

A gas mixture containing 12 per cent. of methyl formate vapour, 35 per cent. of carbon monoxide, 50 per cent. of hydrogen and 3 per cent. of methane is passed at 400 degrees Centigrade and 220 atmospheres, over a contact mass prepared by mixing 2 parts of wetted potassium permanganate with 1 part of zinc chromate and 1 part of copper chromate. Large quantities of a product resembling that of Example 3, but with a higher percentage of free and bound acids is obtained.

EXAMPLE 5.

A tube-shaped reaction vessel, capable of resisting high pressure is supplied with catalyst grains, consisting of 5 parts, by weight, of cadmium oxide, 2 parts, by weight, of copper oxide, and 2 parts by weight of vanadic acid, and a gas mixture composed of 3 volumes of hydrogen and one volume of carbon monoxide is then passed through, at 500 degrees Centigrade and a pressure of 200 atmospheres. The gases leaving the catalyst, containing methanol vapours and unaltered hydrogen and carbon monoxide are passed, while still hot, through a second contact tube, directly adjoining the first one, which is kept at the same temperature, and filled with a contact mass, prepared from 2 parts, by weight, of caustic potash, 2 parts of thallium oxide and 3 parts of potassium permanganate. Under the influence of this second contact mass the methanol vapours are, to a considerable extent, transformed into higher molecular compounds, for example isobutanol. The two contact masses may also be brought into one contact tube in the order named.

The composition of the products varies, depending on the temperature, pressure and composition of the gas mixture. With a high percentage of carbon monoxide ample quantities of organic acids, free or in the form of esters, are formed.

EXAMPLE 6.

Water gas, freed from sulphur compounds and from iron carbonyl, is passed with an admixture of 5 per cent., by volume, of vapourised ethyl alcohol of 96 per cent., at between 380 and 400 degrees Centigrade and 200 atmospheres over a contact mass prepared by mixing 2 parts of potassium carbonate, 4 parts of zinc chromate and 1 part of copper oxide. The product obtained is chiefly composed of liquid organic compounds, insoluble in water. When an addition of methyl, or ethyl, formate is made, the yield of the said compounds is increased. It may be of advantage to subdivide the introduction of the ethanol vapour to the water gas, that is by introducing it at several subsequent places.

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. 247,177 but make no claim to what is claimed therein, but subject to this disclaimer what I claim is:—

1. A process for the synthesis of organic compounds containing oxygen consisting in causing carbon monoxide or a gas containing carbon monoxide to act on a vapourised aliphatic alcohol or an ester thereof or both alcohols and esters with the aid of a catalyst containing a constituent of a hydrating nature alone or in conjunction with a hydrogenating constituent and/or an alkali or alkaline earth metal compound, at an elevated temperature and under elevated pressure.

2. A modification of the process claimed in the preceding claiming clause consisting in employing an aldehyde in a vapourised condition and in the presence of hydrogen, instead of an alcohol.

3. A modification of the process hereinbefore claimed consisting in first subjecting a mixture of an oxide of carbon and hydrogen at an elevated temperature and pressure to the action of a methanol-forming catalyst and subsequently exposing the reaction gases containing methanol vapour without separating the latter from the gases, to a second catalytic treatment in the presence of carbon monoxide employing in this second treatment a contact mass in accordance with the first claiming clause and cooling the reaction gases.

4. The process for the synthesis of organic compounds as described in each of the foregoing examples.

Dated this 9th day of March, 1925.

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

Redhill: Printed for His Majesty's Stationery Office, by Love & Malcomson, Ltd.—1927.