[Third Edition.]

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Oxygenated 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 & Soda Fabrik, of Ludwigshafen-on-Rhine, Germany, a company incorporated 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:—

In the Specifications for Letters Patent Nos. 229,714, 229,715 and 227,147, processes have been described whereby it is possible to manufacture methanol by the catalytic reduction of carbon monoxide or carbon dioxide by means of hydrogen at an elevated pressure and temperature while using certain contact masses completely or substantially free from iron nickel and cobalt. The methanol produced is either practically pure or mixed with certain amounts of other oxygenated organic compounds.

The present invention has for its object to produce substantial amounts of the said oxygenated organic compounds of a higher order than methanol.

My foreign correspondents have found that such oxygen derivatives, which are partly readily soluble in water and partly insoluble or difficultly soluble (being of a more oily nature) are produced in predominating quantities, generally together with greater or less quantities of methanol when the gas mixture composed as aforesaid of carbon monoxide or dioxide or both and hydrogen, is passed over a contact mass suitable to form methanol at otherwise similar conditions, but at a diminished speed compared with the minimum speed necessary for the formation of substantially pure methanol. Accordingly the process consists in passing the mixed gases over the catalysts at an elevated temperature and pressure at such a moderate speed as to lead to the predominating formation of oxygenated organic compounds of a higher order than methanol mainly higher alcohols. As in the manufacture of methanol, so in the present case, iron, nickel, or cobalt should be excluded, or practically excluded, from the contact masses as well as from the apparatus, and volatile compounds of the aforesaid metals should also be removed from the gas mixture as carefully as possible. In order to avoid the formation of such compounds within the apparatus, the latter and especially the contact vessel and other parts of the apparatus liable to become hot, should either consist of metals such as copper, silver, aluminium, or suitable alloys therefor, for example copper manganese alloy, or of special steels containing a substantial percentage of chromium, tungsten, vanadium, or molybdenum, or iron or steel apparatus may be lined or covered inside with such metals, for example with a metal sheet, or by electroplating or any other process.

Those of the contact masses suitable for the formation of methanol are also especially adapted to effect the production of oxygenated organic compounds of the higher order which contain substantial amounts of metallic oxides which are non-reducible under the conditions of working, and especially such contact masses as contain alkali metal or more particularly potassium compounds may be used for this special purpose. By non-reducible metallic oxides are meant metallic oxides which are not reduced by hydrogen or carbon-monoxide or mixtures thereof under ordinary or increased pressure, at temperatures up to 550° Centigrade. Likewise, contact masses allowing the use of relatively high tem-

peratures of about from 350 degrees to 500 degrees Centigrade are very suitable for the production of the oily products. The composition of the gas mixture is of minor importance, as gas mixtures containing an excess of hydrogen over the quantity calculated for the production of methanol may be used just as well as gas mixtures containing exactly the calculated quantities of hydrogen and carbon oxide or even an excess of the latter. Nitrogen or gaseous hydrocarbons may also be present.

In order to explain this invention more fully and how the same may be carried out in practice the following examples are given, but the invention is not limited to these examples.

EXAMPLE 1.

A vessel capable of resisting high pressure and lined inside with copper is supplied with 30 kilogrammes of a contact mass prepared by introducing zinc oxide into fused potassium bichromate and subsequently reducing by means of hydrogen at about 450 degrees Centigrade. A gas mixture composed of between 15 and 20 *per cent.*, by volume, of carbon monoxide and about 75 *per cent.*, by volume, of hydrogen and also containing a little nitrogen, carbon dioxide and methane, is then passed through the contact vessel at a pressure of about 200 atmospheres and a temperature of about 480 degrees Centigrade at a speed or velocity of between 20 and 30 cubic metres per hour (calculated on the volume of the gas when cold and reduced to ordinary conditions). When the reaction gases are passed through a refrigerated receiver without releasing the pressure, a liquid is thereby separated out containing, besides certain amounts of methanol substantial quantities of compounds of an oily nature chiefly higher alcohols, also aldehydes and small quantities of amines and liquid hydrocarbons and varying amounts of water, the oily products remaining generally dissolved in the methanol especially in case only a small quantity of water is formed. The mixture may be worked up in any suitable way and may be separated into its several constituents.

The most suitable speed or velocity for the gas mixtures to give the best output of the oily products depends in each particular case on the nature of the catalyst used, on the temperature and the composition of the gas mixture and the pressure employed and the conditions of working that can be easily ascertained by preliminary test experiments.

EXAMPLE 2.

A contact mass is prepared by intimately mixing 10 parts, by weight, of chromium trioxide, 8 parts, by weight, of zinc oxide and 8 parts of baryta, and the gas mixture containing between 25 and 30 *per cent.* by volume of carbon monoxide and between 75 and 70 *per cent.* by volume, of hydrogen is passed over it at a pressure of 180 atmospheres and between 450 and 500 degrees Centigrade. When 700 grammes of the contact mass aforementioned are used, the speed or velocity of the gas mixture should be between 1 and $1\frac{1}{2}$ cubic metres per hour calculated for ordinary conditions. The liquid collected in the receiver when freed from methanol by fractional distillation consists of an oil containing about 80 *per cent.* of compounds which are insoluble or difficultly soluble in water and chiefly consists of higher alcohols.

EXAMPLE 3.

By passing a gas mixture such as employed in the foregoing Example 2, through 100 grammes of a contact mass prepared from 5 parts, by weight, of tungstic acid, 2 parts by weight of copper oxide and 3 parts by weight of lead oxide at 480 degrees Centigrade and at about 200 atmospheres pressure and with a speed or velocity of 300 litres per hour, (calculated for a gas reduced to ordinary conditions) a substantial quantity of higher alcohols of an oily character, and other oily compounds are produced besides methanol. Should, however, the speed of the gas mixture be 5000 litres per hour, the result would be practically pure methanol.

EXAMPLE 4.

A tube capable of resisting high pressure and lined with an inner tube of copper manganese alloy (containing about 5 *per cent.* manganese) is supplied with a contact mass prepared from 25 parts, by weight, of ammonium bichromate, 16 parts, by weight, of zinc oxide and 28 parts by weight of potassium carbonate, care being taken that the mass is practically free from iron compounds. The contact mass is preferably heated from about 450 to 500 degrees Centigrade before it is filled into the contact tube. Through the latter a mixture of carbon monoxide and hydrogen containing between 50 and 60 *per cent.* of carbon monoxide is then passed at a pressure of 180 atmospheres and between 450 and 500 degrees Centigrade with a speed of 2.4 cubic metres (calculated on gas at ordinary conditions) per hour for

each kilogramme of contact mass contained in the contact vessel. The oily product collected in the receiver contains about 60 *per cent.* compounds insoluble in water and chiefly consisting of higher alcohols.

EXAMPLE 5.

30 kilogrammes of a contact mass obtained by introducing zinc oxide into molten sodium bichromate and afterwards reducing with a mixture of carbon monoxide and hydrogen, are filled into a contact furnace capable of resisting the pressure and lined inside with copper. A gas mixture consisting of 25 *per cent.* to 30 *per cent.* of carbon monoxide and about 45 *per cent.* to 50 *per cent.* of hydrogen, the rest of the gas mixture consisting of nitrogen, carbon dioxide and methane, is passed through this contact mass at a temperature of 480 degrees Centigrade while employing a pressure of 200 atmospheres, with a speed of from 20 to 30 cubic metres per hour (calculated for a cold gas reduced to ordinary conditions). A mixture is separated in the cooled receiver containing, besides methyl alcohol and water, about 50 *per cent.* to 70 *per cent.* of oily products.

By increasing the speed of the gas current to from 800 to 1000 cubic metres per hour and preferably lowering the temperature of the contact mass to 380 degrees to 400 degrees Centigrade, a methanol is obtained in the receiver containing only 2 *per cent.* to 5 *per cent.* of oily products.

EXAMPLE 6.

A mixture of carbon monoxide and hydrogen with 25 *per cent.* to 30 *per cent.* of carbon monoxide is passed at a temperature of from 500 degrees to 520 degrees Centigrade and at a pressure of 180 atmospheres over 350 kilograms of a contact mass prepared by intimately mixing 8 parts of zinc oxide, 10 parts of chromic trioxide and 11.5 parts of manganese carbonate. The speed of the gas current amounts to 3000 to 5000 cubic-metres per hour, calculated on reduced gas. The liquid collected in the receiver is a mixture containing 40 *per cent.* to 50 *per cent.* of oily matter. The residue consists of methyl alcohol and water. If a velocity of the gas current of 20,000 cubic metres per hour and a temperature of from 360 to 380 degrees Centigrade is employed, the above mentioned contact mass yields a methyl alcohol containing only 2 *per cent.* of oil.

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 of oxygenated organic compounds of a higher order than methanol which consists in passing a mixture of an oxide of carbon and a gas containing hydrogen at an elevated pressure and temperature over a contact mass capable of reacting with the said gas mixture to form methanol and preferably such masses as contain substantial amounts of a non-reducible metallic oxide, but which are substantially free from iron, nickel and cobalt, the operation being performed at such a moderate speed as to lead to the predominating formation of oxygenated organic compounds of a higher order than methanol mainly higher alcohols.

2. In the process claimed in the foregoing first claiming clause the use of contact masses containing besides the catalytic element, a compound of potassium.

3. In carrying out the process claimed in the preceding first and second claiming clauses, the use of a temperature of between about 350 and 500 degrees Centigrade.

4. As articles of manufacture oxygenated organic compounds of a higher order than methanol, either alone, or mixed with methanol when prepared in accordance with the foregoing claiming clauses.

Dated this 24th day of May, 1924.

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Agents.

Reference has been directed in pursuance of Section 7, Sub-section 4, of the Patents and Designs Acts, 1907 and 1919, to Specification No. 20,488 of 1913.

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