[Fourth Edition.]

AMENDED SPECIFICATION.

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PATENT SPECIFICATION

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COMPLETE SPECIFICATION (AMENDED).

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:—

It is already known that carbon monoxide or dioxide or mixtures of both can be reduced by means of hydrogen at increased pressure and temperature and under the action of certain catalysts so as to form liquid hydrocarbons and, ordinarily, certain amounts of oxygenated organic products such as alcohols, aldehydes, acids and the like.

My foreign correspondents have now found that the valuable oxygenated compounds, and in particular methanol, which up to the present time could only be obtained by charring wood, can be produced with good yields as the sole, or chief, products by the reduction of carbon monoxide or dioxide provided gas mixtures be employed, on the one hand, containing hydrogen in quantities exceeding those of the carbon oxides, i.e. more than one volume of the former to each one volume of the latter, preferably even in quantities corresponding to, or exceeding those calculated according to the equations:—

$$CO + 2H_2 = CH_3.OH$$

and

$$CO_2 + 3H_2 = CH_3.OH + H_2O,$$

and employing at the same time, on the other hand, contact masses containing non-reducible metal oxides or compounds thereof. By non-reducible metal oxides are meant metal oxides which are not reduced by hydrogen or carbon monoxide or mixtures thereof under ordinary or increased pressure at temperatures up to 550° Centigrade. The non-reducible oxides may be employed alone or mixed or compounded together or with other substances, either inert, or acting catalytically, such as those oxides which are reduced by hydrogen or carbon monoxide or mixtures thereof under ordinary or increased pressure at temperatures up to 550° Centigrade or the corresponding metals or with metals of the non-reducible oxides. As instances of contact masses for the purposes of this invention the oxides, hydroxides, or carbonates of the alkali, earth alkali, or earth metals, comprising aluminium, glucinum, zirconium, thorium, cerium, and other rare earth metals, or mixtures or compounds of magnesia, alumina and the like with the oxides of lead, bismuth, thallium, zinc, cadmium, copper, tin, antimony, silicon, boron, titanium, are mentioned. Iron, nickel and cobalt should, however,

be present, if at all, only in small amounts as they may lead to the formation of methane or other hydrocarbons.

The contact masses may be put into the contact furnace without any previous further treatment. As a rule they will be used in the form of grains or lumps and if mixed catalysts are employed intimate mixtures may be prepared in any suitable manner, for example, by simultaneous precipitation or fusion, or by intimately stirring one of the components with the solution, or melt, of the other, and supports, such as asbestos may also be employed.

The gas mixture serving for the reaction may contain a high excess of hydrogen for example one and a half times the calculated quantity by the above equations or a multiple thereof, and besides, it may be purified and dried prior to the reaction.

The desired reaction will ordinarily be carried out between a temperature of about 300 degrees and 600 degrees Centigrade, but in the case of singularly active masses temperatures even below 300 degrees may be used. The pressure will preferably be kept above 50 atmospheres and may be raised to any desired degree. In general, pressure and temperature should be adapted to the kind of the contact mass actually used; in certain cases very high pressures and/or relatively high temperatures are recommended. The operation can be carried out in a circulating system and with recovery of the heat, by which means the supply of heat can be restricted or even be dispensed with. The original composition of the circulating pure gas is maintained by proper addition of fresh gases. If desired, working may be done without circulating, for example by employing several apparatus in series or by using a single apparatus with a hot part, containing the catalyst, and a cold part without a catalyst, in which latter the liquid reaction products condense.

The separation of the methanol and other liquid compounds is best effected without releasing the pressure by cooling, which may be assisted by using arrangements furthering the condensation such for instance as towers filled with Raschig rings or other bodies, and the like, or washing with water or other suitable liquids may be employed.

The following examples will serve to further illustrate how the invention may be carried into effect, but the invention is not limited to these examples as the contact masses, gas mixtures, temperatures, pressure and other conditions may be varied without departing from the scope of the invention.

EXAMPLE 1.

A mixture of 3 parts, by volume, of hydrogen and 1 part, by volume, of carbon monoxide is passed, at a pressure between about 500 and 1000 atmospheres and a temperature of about 550 degrees Centigrade, over a contact mass consisting of potash-lime, or of a mixture of equal parts of caustic potash and alumina. The velocity of the flow of the gases may vary within wide limits and amount for example to between 5 to 200 cubic metres and more, calculated on atmospheric pressure, per hour, for each kilogramme of contact mass. When the gas mixture after the treatment, is cooled under pressure, a liquid condenses consisting of methyl alcohol, which may be mixed with other alcohols and sometimes a little water, but no substantial amount of substances of an oily nature. The remaining gas may be used again directly or after suitable replenishment, for instance, it may be passed through another contact vessel. The proportions of the gas mixture may be different, though the hydrogen should, in any event exceed the carbon monoxide. Instead of, or besides carbon monoxide, carbon dioxide may be used, and besides hydrogen, gaseous or vapourised hydrocarbons for example from about 10 to 20 per cent. of methane, may be present. Inert gases, for example nitrogen, may also be present.

EXAMPLE 2.

A gas mixture composed of about 22 per cent., by volume of carbon monoxide, 3 per cent. of carbon dioxide, 71 per cent. of hydrogen and 4 per cent. of nitrogen, is conveyed at a pressure of about 180 atmospheres and at a temperature of 520 degrees Centigrade over magnesium chromate. The velocity of the flow of the gases may vary within wide limits and amount, for example, to between 5 to 200 cubic metres and more, calculated on atmospheric pressure, per hour for each kilogramme of contact mass. On cooling the reaction gas under pressure, alcohols, chiefly methanol, condense in rich quantity. A granulated mixture of lead chromate with alumina, to which a little caustic potash may be added is also suitable as a catalyst.

EXAMPLE 3.

A gas mixture, dry and purified, consisting, by volume, of about 20 per cent. of carbon monoxide, 3 per cent. of carbon

dioxide, 4 per cent. of methane and ethane, 70 per cent. of hydrogen and 3 per cent. of nitrogen is passed, at a pressure of 800 atmospheres and at a temperature of between 350 degrees and 400 degrees Centigrade, or a contact mass consisting of magnesium, or zinc, oxide and potassium, or rubidium, hydroxide, or carbonate. The velocity of the flow of the gases may vary within wide limits and amount, for example, to between 5 to 200 cubic metres and more, calculated on atmospheric pressure, per hour for each kilogramme of contact mass. The liquid reaction product consists chiefly of methanol.

EXAMPLE 4.

Copper oxide is intimately mixed with powdered aluminium and the mass is ignited in the air, or in an atmosphere of an inert gas. An intimate mixture of copper and alumina results which on passing over it a mixture of 9 parts, by volume, of hydrogen and 1 part, by volume, of carbon monoxide, gives rise to excellent yields of methanol. The velocity of the flow of the gases may vary within wide limits and amount for example to between 5 to 200 cubic metres and more, calculated on atmospheric pressure, per hour for each kilogramme of contact mass.

As further examples of contact masses in accordance with this invention, there may also be used mixtures of potassium, caesium or rubidium compounds with an oxide, or oxides of, uranium, aluminium, chromium, manganese, or of rare earth metals, such as cerium, lanthanum, thorium, zirconium, or yttrium; and mixtures, or compounds of zinc oxide with the oxides of aluminium, barium, rare earth metals, chromium, magnesium, manganese, tantalum, titanium, tungsten, or vanadium; other instances of efficient mixtures are antimony oxide with glucinum oxide, also tungsten threads containing thoria, or either metallic molybdenum, or thallium containing alumina.

A very efficient catalyst is obtained by melting 300 parts by weight of potassium dichromate and introducing while stirring 100 parts of zinc oxide which proportions may be varied. On continuing heating, the mass becomes stiff and is then poured on a metal sheet and broken, when cool. It may be put into the contact furnace either directly or after leaching out the alkali salt with water, or after a reduction. Instead of zinc oxide, oxides of other metals, for example manganese, thallium, cerium, uranium, thorium, zirconium, or mixtures of them may be introduced into the melt of potassium dichromate.

Having now particularly described and ascertained the nature of this invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A new process for the manufacture of methanol or other alcohols, which consists in causing carbon monoxide or dioxide, or both, to react with hydrogen, the latter exceeding by volume the oxides of carbon, at an elevated pressure and temperature and under the influence of catalysts containing non-reducible metal oxides, or compounds thereof, as hereinbefore defined, but completely or substantially free from iron, nickel, and cobalt.

2. In the process according to Claim 1, the use of catalysts containing mixtures of a non-reducible oxide with a metal, other than iron, nickel and cobalt.

3. The process of manufacturing methanol substantially as described in the foregoing examples.

4. As an article of manufacture methanol, when prepared according to the foregoing claiming clauses.

Dated this 23rd day of August, 1923.

JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London,
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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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