

PATENT SPECIFICATION

Application Date: Aug. 28, 1923. No. 21,733/23.

227,147

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Complete Left: May 24, 1924.

Complete Accepted: Dec. 29, 1924.

PROVISIONAL 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), to be as follows:—

By the reduction of carbon monoxide or dioxide with hydrogen at an elevated temperature and pressure methanol and other oxygenated organic compounds can be produced, if suitable catalysts are used.

My foreign correspondents have now further found that the beforementioned process can be carried out very advantageously by using contact masses containing mixtures of such oxides of metals of different groups of the periodic system as are not reduced to the metals under the condition of working and with a preponderating quantity of the more basic oxide. Non reducible oxides of the second to the seventh group of the periodic system are especially suitable for such mixed catalysts.

As an example the combination of zinc oxide and chromium oxide with the zinc oxide preponderating may be mentioned; from two to twelve or more molecular weights of zinc oxide may be present for each one molecular weight of chromium oxide. Other suitable combinations according to this invention are the oxides of zinc and uranium, zinc and vanadium, zinc and tungsten, magnesium and molybdenum, cerium and manganese but many others may be combined, with the more basic oxide in a preponderating amount in each case. Other substances, for example metals, may also be present.

The mixed contact masses of the character described may be prepared by intimately mixing the constituents, or by simultaneously precipitating them from solutions of proper salts, or by melting suitable salts together, or in any other suitable way. Supports may also be employed.

It is advisable to keep the contact masses free from iron and nickel, or to allow only comparatively small amounts thereof to be contained therein, also to keep the gas mixture serving for the reaction free from volatile iron and nickel compounds and to so construct the apparatus as to avoid a contamination of the contact mass by iron, making it from copper, for example, or lining it inside with copper.

The contact masses may be employed at temperatures between about 200 degrees and 600 degrees Centigrade, the pressure ranging preferably above 50 atmospheres. The products formed, which may consist of either practically pure methanol, or of a mixture of methanol with oxygenated organic substances of an oily nature, insoluble in water, are preferably separated from the reaction gases by cooling without releasing the pressure, and the residual gases may be again subjected to the catalytic treatment, after adding the gases consumed by the reaction. The mixture of carbon monoxide or dioxide, or both, and hydrogen, which latter preferably should exceed, by volume, the former, may also contain gaseous hydrocarbons, nitrogen or other gases.

Dated this 28th day of August, 1923.

JOHNSONS & WILLCOX,

47, Lincoln's Inn Fields, London.

W.G. 2.

Agents.

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:—

By the reduction of carbon monoxide or dioxide with hydrogen at an elevated temperature and pressure methanol and other oxygenated organic compounds can be produced, if suitable catalysts are used.

My foreign correspondents have now discovered that the beforementioned process can be carried out very advantageously by using for contact masses mixtures of such oxides of metals of different groups of the periodic system as are non-reducible and with a preponderating quantity of the more basic oxide. Non-reducible oxides of the second to the seventh group of the periodic system are especially suitable for such mixed catalysts. 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° C.

As an example the combination of zinc oxide and chromium oxide with the zinc oxide preponderating may be mentioned; from two to twelve or more molecular weights of zinc oxide may be present for each one molecular weight of chromium oxide. Other suitable combinations according to this invention are the oxides of zinc and uranium, zinc and vanadium, zinc and tungsten, magnesium and molybdenum, cerium and manganese but many others may be combined, with the more basic oxide in a preponderating amount in each case. Other substances, for example metals, may also be present.

The mixed contact masses of the character described may be prepared by intimately mixing the constituents, or by simultaneously precipitating them from solutions of proper salts, or by melting

suitable salts together, or in any other suitable way. Supports may also be employed. It is advisable to keep the contact masses free from iron, nickel and cobalt, also to keep the gas mixture serving for the reaction free from volatile iron and nickel compounds and to so construct the apparatus as to avoid a contamination of the contact mass by iron, making it from copper, for example, or lining it inside with copper.

The contact masses may be employed at temperatures between about 200 degrees and 600 degrees Centigrade, the pressure ranging preferably above 50 atmospheres. The products formed, which may consist of either practically pure methanol, or of a mixture of methanol with oxygenated organic substances of an oily nature, insoluble in water, are preferably separated from the reaction gases by cooling without releasing the pressure, and the residual gases may be again subjected to the catalytic treatment, after adding the gases consumed by the reaction. The mixture of carbon monoxide or dioxide, or both, and hydrogen, which latter preferably should exceed, by volume, the former, may also contain gaseous hydrocarbons, nitrogen or other gases.

The following example further describes a method of carrying this invention into effect but the invention is not limited thereto.

A gaseous mixture composed, by volume, of 30 parts of carbon monoxide, 64 parts of hydrogen, 4 parts of nitrogen, 1 part of methane and 1 part of carbon dioxide is conveyed, at a pressure of 200 atmospheres and a temperature of 400 degrees Centigrade, over a contact mass, prepared by mixing, while moist, by weight 90 parts of zinc oxide and 10 parts of chromic acid and reducing the latter to chromium oxide before use by reacting on it with the aforementioned gas mixture under the pressure and temperature referred to, which may be done in the contact vessel itself. The velocity of the flow of the gas may vary within wide limits and amount for example to from 5 to 200 cubic metres and more calculated in atmospheric pressure per hour for each kilogramme of contact mass. The reaction gases on cooling, while still

under pressure, yield a condensate of ample quantities of practically pure methanol.

- The following compounded catalysts may be employed with a similar result:
- 85 parts by weight of zinc oxide impregnated with a solution of 15 parts of vanadium nitrate, or 90 parts of cadmium oxide with 10 parts of chromic acid.
 - Even zinc oxide with only one per cent. of chromic acid is an excellent catalyst.

- 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. The manufacture of methanol or other oxygenated organic compounds which consists in passing a mixture of carbon oxides preferably carbon monoxide and hydrogen at an elevated temperature and pressure and preferably while excluding volatile iron and nickel compounds over a contact mass contain-

ing in an intimate mixture at least two oxides of metals belonging to different groups of the periodic system which oxides are non-reducible to the metal as already defined and with the more basic oxide in a preponderating quantity.

2. The manufacture of methanol and other oxygenated organic compounds by the catalytic reduction of carbon oxides, substantially as described.

3. As articles of manufacture methanol and other oxygenated organic compounds when prepared according to the foregoing claiming clauses.

Dated this 23rd day of May, 1924.

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