PATENT SPECIFICATION

Application Date: July 1, 1925. No. 16,975/25. 263,503
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PROVISIONAL SPECIFICATION.

Improvements in or relating to the Production of Oxygen-containing and other Organic Compounds.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of 8, Waterloo Place, London, S.W. 1, do hereby declare the nature of this invention to be as follows:—

This invention relates more particularly to the production of organic compounds, especially methyl alcohol, formaldehyde, keten, acetic acid, acetone and other oxygenated aliphatic compounds from mixtures of carbon monoxide and hydrogen or industrial or other gases or gaseous mixtures containing the same. It is also applicable for the production of other aliphatic or cyclic compounds such as liquid hydrocarbons, higher alcohols, acids and ketones or mixtures containing some or all of these from said gases or gaseous mixtures.

The history in connection with reactions for chemically combining carbon monoxide and hydrogen in mixtures or gases containing them shows, especially by the important researches of Sabatier and Senderens, that essentially with employment of nickel and similarly acting catalysts, such as iron or cobalt, it is possible to produce methane in a quantitative way, but in spite of the many attempts which were made at various times it was not found possible to obtain methyl alcohol or other aliphatic or cyclic derivatives by such a chemical combination.

An advance along this line was made in 1913—1914 (British Patent Specification of Badische Anilin und Soda-Fabrik 20,488 of 1913) when it was proposed to heat mixtures of or containing carbon monoxide and reduced quantities of hydrogen under high pressure in presence of certain catalysts (or mixtures thereof) such as cerium, chromium, cobalt, manganese, molybdenum, osmium, palladium, titanium, zinc or oxides or other compounds of these metals, with or without addition of a basic compound such for instance, as alkali hydroxide. This process suppressed or more or less reduced the formation of methane, so far as the catalysts proposed were not nickel or like catalysts favouring the formation of methane, and yielded products consisting of mixtures of aliphatic or cyclic compounds such as liquid and gaseous hydrocarbons (saturated and unsaturated), alcohols, aldehydes, ketones, and acids.

The reactions of chemically combining carbon monoxide and hydrogen in mixtures or gases containing them have been developed in recent years for producing methyl alcohol, higher aliphatic alcohols, or other oxygenated aliphatic compounds, and even higher hydrocarbons, by heating the gases under high pressure under modified or selected conditions in regard to the choice of catalysts, relative proportions of the two gases, temperature or other conditions, with the principal aim of attaining a much more commercial formation or yield of these respective useful products.

Thus for instance, in British Specification 227,147 (Badische) it is proposed to manufacture methyl alcohol or other oxygenated organic compounds by passing a mixture of or containing carbon monoxide and hydrogen (the latter preferably in excess by volume) at an elevated temperature and high pressure, and preferably while excluding volatile iron and nickel compounds, over a contact mass containing in an intimate mixture at least two oxides of metals belonging to different groups of the periodic system (e.g. the oxides of zinc and chromium, zinc and uranium, zinc and vanadium, zinc and tungsten, magnesium and

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the catalysts therein referred to, and avoiding the presence of nickel or other catalysts favourable to the formation of methane, the reactions being conducted at or about atmospheric pressure.

The carbon monoxide and hydrogen or gases containing the same may be freed from impurities such for instance as organic compounds of sulphur and volatile iron compounds or other detrimental impurities before being subjected to the reaction.

Any suitable or known vessels or apparatus may be employed for performing the reactions.

Dated this 1st day of July, 1925.

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COMPLETE SPECIFICATION.

Improvements in or relating to the Production of Oxygen-containing and other Organic Compounds.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of 8, Waterloo Place, London, S.W. 1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates more particularly to the production of organic compounds, especially methyl alcohol, formaldehyde, keten, acetic acid, acetone and other oxygenated aliphatic compounds from mixtures of carbon monoxide and hydrogen or industrial or other gases or gaseous mixtures containing the same. It is also applicable for the production of other aliphatic or cyclic compounds such as liquid hydrocarbons, higher alcohols, acids and ketones or mixtures containing some or all of these from said gases or gaseous mixtures.

The history in connection with reactions for chemically combining carbon monoxide and hydrogen in mixtures or gases containing them shows, especially by the important researches of Sabatier and Senderens, that essentially with employment of nickel and similarly acting catalysts, such as iron or cobalt, it is possible to produce methane in a quantitative way, but in spite of the many attempts which were made at various times it was not found possible to obtain methyl alcohol or other aliphatic or cyclic derivatives by such a chemical combination.

An advance along this line was made in 1913—1914 (British Patent Specification of Badische Anilin und Soda-Fabrik 20,488 of 1913) when it was proposed to heat mixtures of or containing carbon monoxide and reduced quantities of hydrogen under high pressure in presence of certain catalysts (or mixtures thereof) such as cerium, chromium, cobalt, manganese, molybdenum, osmium, palladium, titanium, zinc or oxides or other compounds of these metals, with or without addition of a basic compound such for instance, as alkali hydroxide. This process suppressed or more or less reduced the formation of methane, so far as the catalysts proposed were not nickel or like catalysts favouring the formation of methane, and yielded products consisting of mixtures of aliphatic or cyclic compounds such as liquid and gaseous hydrocarbons (saturated and unsaturated), alcohols, aldehydes, ketones, and acids.

The reactions of chemically combining carbon monoxide and hydrogen in mixtures or gases containing them have been developed in recent years for producing methyl alcohol, higher aliphatic alcohols, or other oxygenated aliphatic compounds, and even higher hydrocarbons, by heating the gases under high pressure under modified or selected conditions in regard to the choice of catalysts, relative proportions of the two gases, temperature or other conditions, with the principal aim of attaining a much more commercial formation or yield of these respective useful products.

Thus for instance, in British Specification 227,147 (Badische) it is proposed to manufacture methyl alcohol or other oxygenated organic compounds by passing a mixture of or containing carbon monoxide and hydrogen (the latter preferably in excess by volume) at an elevated temperature and high pressure, and preferably while excluding volatile iron and nickel compounds, over a contact mass containing in an intimate mixture at least two oxides of metals belonging to different groups of the periodic system (e.g. the oxides of zinc and chromium,

zinc and uranium, zinc and vanadium, zinc and tungsten, magnesium and molybdenum, or cerium and manganese), and with the more basic oxide in a preponderating quantity, said metal oxides not being reducible by hydrogen or carbon monoxide or mixtures thereof under ordinary or increased pressure at temperatures up to 550° C.

Again, according to another British Specification 229,714 (Badische) it is proposed to manufacture methyl alcohol or other oxygenated organic compounds by causing carbon monoxide to react with hydrogen (the latter in excess by volume) at an elevated pressure and temperature under the influence of catalysts containing non-reducible metal oxides (i.e. non-reducible by hydrogen or carbon monoxide or their mixtures under ordinary or increased pressure at temperatures up to 550° C.) or compounds thereof, completely or substantially free from iron, nickel or cobalt, said metal oxides being associated or not with a metal other than iron, nickel and cobalt. Numerous examples of catalysts or catalytic mixtures which may be employed are indicated in said specification, viz. 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 or titanium.

Again in another British Patent Specification 229,715 (Badische) it is proposed to produce methyl alcohol or products consisting substantially of methyl alcohol by catalytically reducing carbon monoxide with hydrogen at elevated temperature and pressure by the use of contact masses containing, besides one or more of the elements, copper, silver, gold, zinc, cadmium and lead, also titanium, vanadium, chromium, manganese and other cognate elements related to them, viz. zirconium, cerium, thorium, niobium, tantalum, molybdenum, tungsten, uranium, or boron, or more than one of these elements, or compounds thereof, the gas mixtures employed preferably containing more hydrogen by volume than carbon monoxide, and it being stated that such gas mixtures should be used in any case when mixtures of zinc with oxides of chromium, manganese, molybdenum, titanium, or cerium are used as catalysts. It is further stated that the catalysts employed should be free from alkali compounds and from iron and nickel.

In the Specification of a previous application of mine No. 15,392/1925 (262,494) I have described how methyl alcohol may be produced under heat and pressure from mixtures of or containing hydrogen and carbon monoxide in appropriate proportions, with the aid of zinc oxide as catalyst.

In the Specification of another Application No. 15,394/1925 (262,832) I have described how acetic acid may be produced under heat and pressure from mixtures of or containing hydrogen and carbon monoxide in appropriate proportions, with employment of suitably chosen catalysts or substances such as therein indicated, said catalysts not being those known to favour the formation of methane.

In the Specification of another Application No. 15,396/1925 (262,364) I have described how keten may be produced under heat and pressure from mixtures of or containing hydrogen and carbon monoxide in appropriate proportions with the aid of suitable catalysts, such catalysts not being those known to favour the formation of methane.

In all the processes described in my said previous specifications and in the processes of the previous publications hereinbefore referred to the reactions are performed under high pressures.

I have now found that by employing the catalysts indicated in my said respective previous specifications and avoiding the employment of catalysts favourable to the formation of methane from carbon monoxide and hydrogen, such as nickel, iron and cobalt, it is possible to produce the products of the processes of my said respective specifications at ordinary atmospheric pressure without formation of methane or with formation of only very small quantities of methane. And I have further found that by avoiding employment of catalysts such as referred to favourable to the formation of methane, and employing the catalysts indicated in the other British Patent Specifications 20,488/1913, 227,147, 229,714, and 229,715 hereinbefore referred to, it is likewise possible to obtain the products of these processes at ordinary atmospheric pressure with formation of no methane or but little methane.

This is a very surprising discovery, since it has hitherto always been supposed that high pressures are an essential condition for the production of methyl alcohol, formaldehyde and other products than methane, by reactions of carbon monoxide with hydrogen.

The processes may be performed substantially as described in the specifica-

tions referred to respectively, using the catalysts therein referred to, and avoiding the presence of nickel or other catalysts favourable to the formation of methane, the reactions being conducted at or about atmospheric pressure, the other conditions, such as proportions and temperature, being the same as those indicated in the aforesaid specifications.

The carbon monoxide and hydrogen or gases containing the same may be freed from impurities such for instance as organic compounds of sulphur and volatile iron compounds or other detrimental impurities before being subjected to the reaction.

Any suitable or known vessels or apparatus may be employed for performing the reactions.

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. Process for the production of oxygen-containing organic compounds or higher hydrocarbons by subjecting gaseous mixtures of or containing carbon monoxide and hydrogen to the action of heat in the presence of a catalyst capable of combining carbon monoxide and hydrogen to form methyl alcohol or other oxygenated organic compounds (excluding catalysts capable of forming methane or substantial quantities of methane), characterised in that the combination of the carbon monoxide and hydrogen is effected at about atmospheric pressure.

2. Process for the manufacture of methyl alcohol, formaldehyde, keten, acetic acid, acetone or other oxygen containing organic compounds or higher hydrocarbons from carbon monoxide and hydrogen, substantially as described.

3. Methyl, alcohol, formaldehyde, keten, acetic acid, acetone or other oxygen-containing organic compounds or higher hydrocarbons when prepared or produced by the processes herein described and claimed.

Dated this 20th day of April, 1926.

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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 Specifications Nos. 179,951, 157,047 and 108,855.

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