[Third Edition.]

# PATENT SPECIFICATION

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## PROVISIONAL SPECIFICATION.

## Improvements in or relating to the Manufacture of Oxygenated Organic Compounds.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of Celanese House, 22 & 23, Hanover Square, London, W. 1, do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of organic compounds and particularly of oxygenated organic compounds from oxides of carbon and hydrogen, or alternatively from compounds synthesised therefrom, e.g. methyl alcohol, mixed or not with oxides of carbon and/or hydrogen.

According to the present invention oxygenated organic compounds are produced by the catalytic hydrogenation of carbon monoxide or carbon dioxide or mixtures thereof in presence of iron, cobalt and nickel in the form of their borates, silicates and phosphates or salts of other oxy-acids of phosphorus.

The said iron, nickel and cobalt catalysts alone or in admixture with each other may be employed according to the present invention in conjunction with copper, the presence of the copper, even in small proportions, exercising a favourable influence upon the reaction. Alternatively or in addition, as hereinafter referred to, the reaction may be carried out in copper vessels or in copper lined vessels. The catalysts or catalyst mixtures of the present invention may furthermore be used in admixture or in association with the catalysts of my co-pending Application No. 22,779/29 (Serial No. 337,014) i.e. alkali or alkaline earth ferrites, ferrates, cobaltates or cobaltites.

It is advantageous for the product of the oxygenated compounds, of a higher order than methyl alcohol, particularly contemplated by the present invention, to use the iron, cobalt or nickel catalysts of the present invention in association or chemical combination with metals of the alkali or alkaline earth series, for example sodium, potassium, calcium, barium and magnesium. The alkali and alkaline earth metals may be present in any desired proportion in relation to the iron, cobalt or nickel. For example they may be present in a proportion of 1 equivalent of the alkali or alkaline earth metal to 2 equivalents of iron, cobalt and nickel, but improved results are obtainable by using them in a relatively higher proportion such as 1, 1½ or 2 or more equivalents of alkali or alkaline earth metal to 1 equivalent of iron, cobalt and nickel.

Double salts (i.e. borates, silicates or phosphates or salts of other oxyacids of phosphorus) of the alkali or alkaline earth metals and the iron, cobalt or nickel may be employed.

Initially the iron, cobalt or nickel are present in the form of a salt of any of the oxy acids of boron, silicon or phosphorus; for example in the form of ortho, pyro or meta phosphates or in the form of phosphites or hypophosphites or in the form of ortho or meta silicates.

Such compounds may contain the metal and the acid radicle in any convenient proportion, but it is found that by using a salt containing the acid radicle in an excess over that chemically equivalent to the metal, particularly advantageous results are obtainable. Where such compounds are acid salts such as acid phosphates, acid silicates, and the like they may be produced in any convenient manner. For instance they may be produced by a partial neutralisation of the acid or they may be produced either previous to or during the reaction by simple heating of a complex metallo ammonium salt of the acid, for example a complex metallo ammonium phosphate. In place of an acid salt, a normal salt in admixture with the acid may be used.

Reacting gases of varying composition may be employed for the purpose of the present invention, for example reacting gases containing two volumes of carbon monoxide or dioxide to one volume of hydrogen, or equal volumes of carbon monoxide or dioxide and of hydrogen, or one volume of carbon monoxide or dioxide to two volumes of hydrogen. Mixtures containing intermediate proportions of carbon monoxide or dioxide and hydrogen may be employed, or mixtures containing the reacting gases in proportions outside the limits indicated above. Mixtures of carbon monoxide and dioxide may of course be employed.

The reaction according to the present invention may be conducted at any suitable temperature for the synthesis of organic compounds, for example temperatures ranging from 200° to 250° C. to 400° to 500° or even 600° C. or more, but preferably temperatures are used between 250° and 400° C., and particularly between temperatures of 250° to 300° to 350° C. The reaction is preferably carried out under pressure, for example pressures of 50, 100, 200, 300 or 500 atmospheres or more.

I have further found that the catalysts or catalyst mixtures of the present invention may be employed for the production of further oxygenated organic compounds from compounds, e.g. methyl or ethyl alcohol or other alcohols, obtainable from oxides of carbon and hydrogen. The methyl alcohol or other compounds indicated may be used alone or in conjunction with carbon monoxide, carbon dioxide and/or hydrogen. In this modification of the invention methyl alcohol, for example, may be converted into compounds of a higher order, for example into ethyl alcohol, acetaldehyde, acetic acid, etc. The vapours of the methyl alcohol or other compound may be passed with or without carbon monoxide or dioxide and with or without hydrogen over the catalysts of the invention contained in a heated reaction vessel. The carbon monoxide or dioxide and/or hydrogen, if used, may be mixed with methyl alcohol vapour in any desired manner, for example such a mixture may be prepared by bubbling the gases through a heated vessel containing methyl alcohol, or alternatively the methyl alcohol may be sprayed into a current of the gas. The methyl alcohol or other compound may be prepared in a preliminary operation continuously with its use according to the present invention for the production of higher oxygenated organic compounds. Mixtures of carbon monoxide or carbon dioxide and hydrogen or gases containing such mixtures may be passed through a reaction chamber containing zinc oxide or basic zinc chromate or other catalysts or catalyst mixtures capable of producing methyl alcohol, and the resulting gas or vapours passed directly over the catalysts or catalyst mixtures of the present invention. Instead of using methyl alcohol or other compound obtainable from carbon monoxide or dioxide and hydrogen, compounds capable of yielding the methyl alcohol, etc., may be used, for example methyl formate, methyl acetate or dimethyl ether.

In the present invention it is not of course necessary to utilise pure reacting gases. Mixtures containing the desired reacting gases may be employed, for example coke oven gas, producer gas, water gas and the like. The proportions of reacting gases in such industrial gases may be adjusted if desired by suitable additions. The reacting gases may contain inert gases such as nitrogen, or they may contain hydrocarbons for example methane. The presence of methane or other paraffin or other hydrocarbons forms an important feature of the present invention. The methane or the like, may, if desired, wholly or partly replace the hydrogen or may be used in addition thereto.

The reactions according to the present invention may be carried out in any suitable reaction chambers. As referred to above the use of copper chambers or copper lined chambers presents advantages, but steel chambers, and particularly steel containing molybdenum, tungsten, manganese, cobalt, nickel or the like, may also be used.

Dated this 24th day of July, 1929.

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## COMPLETE SPECIFICATION.

## Improvements in or relating to the Manufacture of Oxygenated Organic Compounds.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of Celanese House, 22 & 23, Hanover Square, London, 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 to the manufacture of oxygenated organic compounds from oxides of carbon and hydrogen, or alternatively from compounds synthesised therefrom, e.g. methyl alcohol, mixed or not with oxides of carbon and/or hydrogen.

According to the present invention oxygenated organic compounds are produced by the catalytic hydrogenation of carbon monoxide or carbon dioxide or mixtures thereof in presence of iron, cobalt and nickel in the form of their borates, silicates and phosphates or salts of other oxy-acids of phosphorus.

The said iron, nickel and cobalt catalysts alone or in admixture with each other may be employed according to the present invention in conjunction with copper, the presence of the copper even in small proportions, exercising a favourable influence upon the reaction. Alternatively or in addition, as hereinafter referred to, the reaction may be carried out in copper vessels or in copper lined vessels. The catalysts or catalyst mixtures of the present invention may furthermore be used in admixture or in association with the catalysts of my co-pending Application No. 22,779/29 (Serial No. 337,014), i.e. alkali or alkaline earth or other ferrites, ferrates, cobaltates or cobaltites.

It is advantageous for the production of the oxygenated compounds, of a higher order than methyl alcohol, particularly contemplated by the present invention, to use the iron, cobalt or nickel catalysts of the present invention in association with metals of the alkali or alkaline earth series, for example sodium, potassium, calcium, barium and magnesium. These alkali and alkaline earth metals may be present in any desired proportion in relation to the iron, cobalt or nickel. For example they may be present in a proportion of 1 equivalent of the alkali or alkaline earth metal to 2 equivalents of iron, cobalt and nickel, but improved results are obtainable by using them in a relatively higher proportion such as 1, 1½ or 2 or more equivalents of alkali or alkaline earth metal to 1 equivalent of iron, cobalt and nickel. Double salts (i.e. borates, silicates or phosphates or salts of other oxy acids of phosphorus) of the alkali or alkaline earth metals and the iron, cobalt or nickel may be employed.

Initially the iron, cobalt or nickel are present in the form of a salt of any of the oxy acids of boron, silicon or phosphorus; for example in the form of ortho, pyro or meta phosphates or in the form of phosphites or hypophosphites or in the form of ortho of meta silicates.

Such compounds may contain the metal and the acid radicle in any convenient proportion, but it is found that by using a salt containing the acid radicle in an excess over that chemically equivalent to the metal, particularly advantageous results are obtainable. Where such compounds are acid salts such as acid phosphates, acid silicates, and the like they may be produced in any convenient manner. For instance they may be produced by a partial neutralisation of the acid or they may be produced either previous to or during the reaction by simple heating of a complex metallo ammonium salt of the acid, for example a complex metallo ammonium phosphate. In place of an acid salt, a normal salt in admixture with the acid may be used, or for instance there may be employed other compounds of the metals with the acids referred to and having an excess of acid radicle over the metal radicle, as for instance ferric silicate, e.g. the mineral anthosiderite $2Fe_2O_39SiO_2$, nickel octaborate, cobalt octaborate.

Reacting gases of varying composition may be employed for the purpose of the present invention, for example reacting gases containing two volumes of carbon monoxide or dioxide to one volume of hydrogen, or equal volumes of carbon monoxide or dioxide and of hydrogen, or one volume of carbon monoxide or dioxide to two volumes of hydrogen. Mixtures containing intermediate proportions of carbon monoxide or dioxide and hydrogen may be employed, or mixtures containing the reacting gases in proportions outside the limits indicated above. Mixtures of carbon monoxide and dioxide may of course be employed.

The reaction according to the present invention may be conducted at any suitable temperature for the synthesis of organic compounds, for example temperatures ranging from 200° to 250° C. to 400° to 500° or even 600° C. or more, but preferably temperatures are used between 250° and 400° C., and particularly between temperatures of 250° to 300° to 350° C. The reaction is preferably carried out under pressure, for example pressures of 50, 100, 200, 300 or 500 atmospheres or more.

I have further found that the catalysts or catalyst mixtures of the present invention may be employed for the production of further oxygenated organic compounds from compounds, e.g. methyl or ethyl alcohol or other alcohols, obtainable from oxides of carbon and hydrogen. The methyl alcohol or other compounds indicated may be used alone or in conjunction with carbon monoxide, carbon dioxide and/or hydrogen. In this modification of the invention methyl alcohol, for example, may be converted into compounds of a higher order, for example into ethyl alcohol, acetaldehyde, acetic acid, etc. The vapours of the methyl alcohol or other compound may be passed with or without carbon monoxide or dioxide and with or without hydrogen over the catalysts of the invention contained in a heated reaction vessel. The carbon monoxide or dioxide and/or hydrogen, if used, may be mixed with methyl alcohol vapour in any desired manner, for example such a mixture may be prepared by bubbling the gases through a heated vessel containing methyl alcohol, or alternatively the methyl alcohol may be prepared into a current of the gas. The methyl alcohol or other compound may be prepared in a preliminary operation continuously with its use according to the present invention for the production of higher oxygenated organic compounds. Mixtures of carbon monoxide or carbon dioxide and hydrogen or gases containing such mixtures may be passed through a reaction chamber containing zinc oxide or basic zinc chromate or other catalysts or catalyst mixtures capable of producing methyl alcohol, and the resulting gas or vapours passed directly over the catalysts or catalyst mixtures of the present invention. Instead of using methyl alcohol or other compound obtainable from carbon monoxide or dioxide and hydrogen, compounds capable of yielding the methyl alcohol, etc., may be used, for example methyl formate, methyl acetate or dimethyl ether.

In the present invention it is not of course necessary to utilise pure reacting gases. Mixtures containing the desired reacting gases may be employed, for example coke oven gas, producer gas, water gas and the like. The proportions of reacting gases in such industrial gases may be adjusted if desired by suitable additions. The reacting gases may contain inert gases, such as nitrogen, or they may contain hydrocarbons for example methane. The presence of methane or other paraffins or other hydrocarbons forms an important feature of the present invention. The methane or the like, may, if desired, wholly or partly replace the hydrogen or may be used in addition thereto.

The reactions according to the present invention may be carried out in any suitable reaction chambers. As referred to above the use of copper chambers or copper lined chambers presents advantages, but steel chambers, and particularly steel containing molybdenum, tungsten, manganese, cobalt, nickel, or the like, may also be used.

The following examples serve to illustrate convenient forms of execution of the invention, it being understood that they are given only by way of illustration and are in no way limitative.

### EXAMPLE 1.

Water gas containing about 30% carbon monoxide and 65% hydrogen is passed under a pressure between about 100 and 200 atmospheres in contact with a catalyst composed of one or more of the following compounds heated to a temperature between 250° and 400° C., viz:—

Cobalt octaborate
Nickel octaborate
Cobalt magnesium borate $(2B_2O_3(CoOMgO)_3)$
Ferric meta phosphate
Ferric silicate (e.g. anthosiderite $2Fe_2O_3 9SiO_2$)

There results a copious yield of ethanol and higher alcohols together with aldehydes and acids.

### EXAMPLE 2.

Methanol or a mixture of methanol and carbon monoxide, carbon dioxide or hydrogen is passed under a pressure of between about 100 and 200 atmospheres in contact with a catalyst composed of one or more of the metal compounds referred to in Example 1 heated to a temperature between 250° and 400° C. There likewise results a copious yield of ethanol and higher alcohols. In the case where methanol is employed alone or in conjunction with carbon monoxide or dioxide (and particularly carbon dioxide) acetaldehyde, acetic acid and higher acids, aldehydes and esters appear in the product. When, however, hydrogen is employed in conjunction with the methanol the aldehydes, acids and esters are substantially absent from the product.

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 manufacture of oxygenated organic compounds and particularly ethanol and higher aliphatic alcohols from mixtures of hydrogen and oxides of carbon, characterised in that the reaction is performed in presence of a catalyst consisting of iron, nickel or cobalt in the form of their borates, silicates, phosphates or salts of other oxy-acids of phosphorus.

2. Process according to claim 1 and wherein the said metals are used in association with metals of the alkali or earth alkali series.

3. Process according to claim 1 or 2 and wherein the said metals are employed in the form of the said compounds containing an excess of acid radicle over the chemical equivalent of the metal.

4. Process according to claim 1, 2 or 3 and wherein the reaction is performed at temperatures between 200° and 600° C. and especially between 250° and 400° C.

5. Process according to claim 1, 2, 3

or 4 and wherein the reaction is performed under pressures of 50—200 or more atmospheres.

6. Modification of the process according to any of the preceding claims, characterised in that there is employed instead of the mixture of hydrogen and oxides of carbon oxygenated organic compounds obtainable by synthesis from oxides of carbon and hydrogen, and especially methanol, ethanol, or other aliphatic alcohols, the oxygenated organic compounds being employed in presence or absence of carbon monoxide, carbon dioxide and/or hydrogen.

7. Process for the manufacture of oxygenated organic compounds substantially as described in Example 1.

8. Process for the manufacture of oxygenated organic compounds substantially as described in Example 2.

9. Process for the manufacture of oxygenated organic compounds substantially as hereinbefore described.

10. Oxygenated organic compounds whenever prepared by the process claimed in any of the preceding claims.

Dated this 20th day of May, 1930.

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